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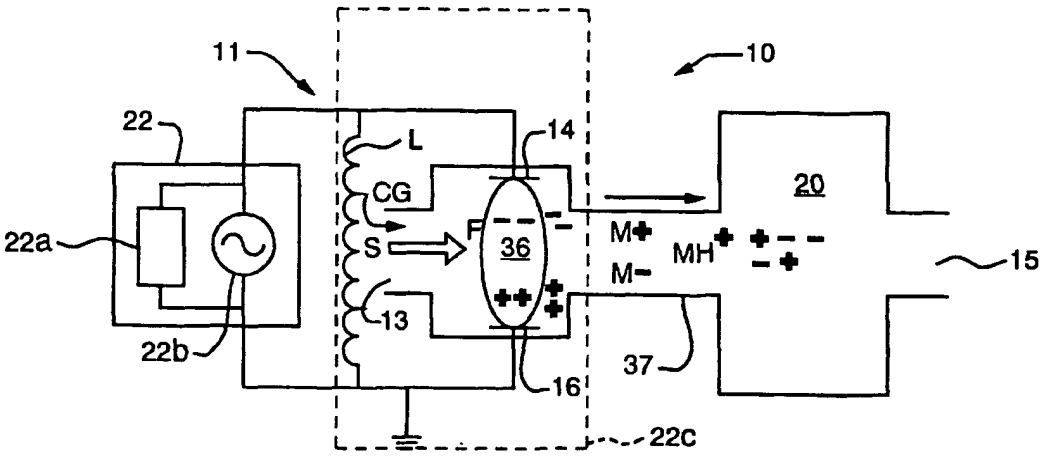

(57) Abstract: In a system (10) for chemical analysis, an RF-driven plasma ionization device (11) including a pair of spaced-apart and plasma-isolated electrodes (14, 16), the electrodes (14, 16) are connected to a power source (22) wherein the electrodes (14, 16) act as plates of a capacitor of a resonant circuit (22c), the gas (S) electrically discharges and creates a plasma of both positive and negative ions, and the voltage is applied as a continuous alternating waveform or as a series of pulses, such as a packet waveform.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

CAPACITIVE DISCHARGE PLASMA ION SOURCE

BACKGROUND OF THE INVENTION:

The present invention relates to an ionization source, and more particularly, to a gas-discharge ionizer.

Creation of ionized particles is a useful tool for many applications, such as for ignition of lasing or to assist chemical analysis, among other uses. In some equipment, high energy radioactive sources of alpha or beta particles are employed for the ionization process. However, because of their potential health hazard, wide-spread use of equipment using radioactive ionization sources in many applications has been limited. Equipment such as gas analyzers, among other equipment, that uses radioactive sources are therefore limited in their utility. While some smoke alarms use radioactive sources, the amount of ionization is low, and still requires government regulation.

Photo-ionization and UV ionization techniques are employed as alternatives to use of a radioactive ionization source. These ionization approaches have relatively low ionization energies, typically 8-11 eV, which limits the types of molecules that can be ionized. Also these devices are typically delicate and fragile, and hence are generally not suitable to operate in harsh environments or in applications requiring a significant amount of manual handling. Furthermore, UV devices require some maintenance and the intensity degrades overtime. As such, even though photo-ionization and UV ionization devices are typically safer to operate than radioactive ionization sources, they are not a viable or cost-effective option in many circumstances, whether for general equipment use or for gas analyzers.

Corona discharge is another source of non-radioactive ionization. It provides high energy in a compact package. However, this process is not stable and often-times contaminates the sample, as would interfere with analytical results. Furthermore, the generated ion species depends upon the applied voltage.

RF discharge ionization reduces some of these disadvantageous effects. RF discharges are subdivided into inductive and capacitive discharges, differing in the way the discharge is produced.

Inductive methods are based on electromagnetic induction so that the created electric field is a vortex field with closed lines of force. Inductive methods are used for high-power discharges, such as for production of refractory materials, abrasive powders, and the like. In PCT publication number WO 01/69220, an inductively coupled plasma ionization technique is disclosed. Ions produced within the plasma source are provided to a high Field Asymmetric Waveform Ion Mobility Spectrometry (FAIMS) analyzer within a low pressure chamber of a mass spectrometer and in fluid communication with the plasma source for receiving ions therefore. The ions are separated in the FAIMS and at least some of the ions are provided to the mass spectrometer after separation. Inductively coupled ionization sources, such as described in WO 01/69220, tend to be power consuming, and further, the inductively coupled ionization sources are relatively complex, large and expensive.

Capacitive discharge methods are used to maintain RF discharges at moderate pressures $p\sim$ 1-100 Torr and at low pressures $p\sim 10^{-3}$ - 1 Torr. The plasma in them is weakly ionized and non-equilibrium, like that of a corona discharge. Moderate-pressure discharges have found application in laser technology to excite CO_2 lasers, while low-pressure discharges are used for ion treatment of materials and in other plasma technologies. Varieties of radio-frequency capacitive discharge are discussed in Raizer, Shneider and Yatsenko, entitled Radio-Frequency Capacitive Discharges, © 1995 CRC Press LLC, with general background at pages 1-3.

In PCT publication number WO 96/19822, an RF ion source providing capacitively coupled ionization is described. The RF ion source is suitable for low power operation over a range of pressures in air. The source includes anode and cathode electrodes connected to an RF signal supply. The anode is adapted to provide a surface area over which a plasma discharge may occur. In this way, the anode presents no more useful surface than is required to accommodate the optimum area of the plasma discharge, preventing plasma wander and enhancing the stability of the discharge over known ion sources. The ion source provides an

effective discharge with very low power even at atmospheric pressure.

Capacitively coupled ionization sources, such as described in WO 96/19822, are more efficient than inductively coupled ionization sources but may contaminate the sample due to electrode surface contact with the gas sample and plasma, leading to secondary ion emissions. The gas sample may corrode the electrode surface, and electrons freed from the plasma molecules, produced by the gas sample interaction with the electric field between the electrodes, can strike the electrode plates and are removed from the plasma, thus causing the plasma to have a net positive charge and an average potential relative to the plates. This drives the ions with a high velocity into the electrodes and can lead to the release of electrode plate molecules from the electrode surface. Also, the chemicals in the gas sample or plasma can chemically react with or corrode the electrodes, which can contaminate the sample. This can cause chemical analysis errors.

In view of the foregoing, there is a felt need for a clean and stable ionization source that is compact, light-weight and inexpensive and delivers a relatively high level of ionization energy for analytical applications in gas (e.g., air) at pressures including atmospheric pressure.

It is therefore an object of the present invention to provide a clean and stable, non-radioactive, ionization source.

It is another object of the present invention to provide a clean and stable, non-radioactive, robust, ionization source that is suitable for analytical applications and the like.

It is a still another object of the present invention to provide a clean and stable, non-radioactive, robust, ionization source that is compact, light-weight and inexpensive and delivers a relatively high level of ionization energy for analytical applications and the like in gas (e.g., air) at pressures including atmospheric pressure.

It is a further object of the present invention to provide a clean and stable, non-radioactive, robust, ionization source that provides positive and negative ions simultaneously.

SUMMARY OF THE INVENTION:

The present invention meets the need for non-radioactive ionization sources. More specifically, we have discovered an RF-driven capacitive discharge method and apparatus for generation of a high energy, clean and stable plasma for sample ionization. A preferred embodiment of the invention is useful as an ionization source for chemical analysis and other applications and is operable in gas (e.g., air) at pressures including atmospheric pressure.

One embodiment of the invention provides a capacitive discharge apparatus that generates a clean and stable plasma in gas (e.g., air) at pressures including at or around atmospheric pressure. The apparatus includes two electrodes spaced by a gap. A plasma is formed in the gap.

In various embodiments of the invention, either one or both of the electrodes is isolated from the plasma environment. More particularly, to reduce or prevent electrode surface molecular discharge and to limit or prohibit ion contamination, a low or non-conductive material, whether an insulator or dielectric, is used to isolate the electrodes. This protects the electrodes from corrosion and electron impact.

Therefore a plasma generator apparatus of the invention is able to ionize a wide range of compounds without contamination from electrode surface molecular discharge and ion contamination. A preferred embodiment of the invention provides a clean and stabilized plasma generator with both electrodes being insulated from the plasma environment. However, good results may also be obtained in practice of the invention when one only of the electrodes is insulated.

In addition to the foregoing, a high power RF electric field is applied to the electrodes to generate the plasma in the gap by use of a resonant circuit. The RF-driven and isolated electrodes produce a stable plasma and have a long service life, producing little or no contaminants in the plasma.

In operation, when a carrier gas and a chemical sample are introduced into the plasma, the gas, such as air, and the sample, are ionized and are passed downstream for further processing. It is a further benefit that the invention can produce plasma having both positive and negative ions.

The present invention allows control of energy imparted to the plasma. In one case, we can generate a plasma, preferably by "soft" atmospheric pressure ionization (API); in another case we can increase of the energy into the plasma and perform hard ionization. It will be appreciated that ionization may be characterized as "soft" or "hard" depending on the electric field energy pumped into the gas discharge. Soft ionization involves charge attraction and transfer reactions and produces molecular ions, and is non-destructive. Hard ionization results from electron impact and produces fragment ions. Both types of ionization may be useful in practice of the invention. For example, soft ionization may be selected for analysis of in-tact ionized molecules, while fragmentation may generate additional useful data when complex mixtures are analyzed.

In a preferred embodiment, we use a high efficiency drive circuit to stabilize the plasma. In one embodiment we use a resonant drive circuit to produce a high frequency (RF) high voltage for increased discharge stability and decreased power consumption. In a preferred embodiment, we use a resonant circuit with system stability provided via negative feedback. In another embodiment, additional operating efficiency is achieved by using a pulsed high frequency high voltage drive.

Various electrode configurations are within the spirit and scope of the invention, including planar, cylindrical, curved, molded, wire, and needle shapes which present any variety of flat or curvilinear ionization surfaces. The electrodes may be parallel or at an angle to each other. In one embodiment, the gas sample flows between the electrodes, and in another embodiment, the gas sample flows around the electrodes.

Among other advantages, the capacitively coupled ionization device of the present invention is clean and stable, robust, light-weight, compact, and can operate at, above and below atmospheric pressure. It is highly efficient and cost-effective and provides high ionization intensities that are practical for a wide range of applications, such as, but not limited to, gas analysis, while consuming low power. The isolated electrodes produce a stable plasma and have a long service life, producing little or no contaminants in the gas sample.

Since the device is operable in a common RF frequency range and is a non-radioactive source, it does not have to be federally regulated as in the manner of radioactive sources, and

hence can be conveniently used in a wide range of applications. Thus embodiments of the present invention therefore meet the need for non-radioactive ionization sources and overcomes the inadequacy of known inductive and capacitive ionization sources to provide clean and stable ionization sources for generation of charged particles, such as is useful for gas analysis and other applications.

The present invention includes the innovations of commonly assigned and owned provisional applications referred to as Attorney Docket M008, entitled Miniature Atmospheric Pressure Capacitive Discharge Ionization Source, By Raanan A. Miller and Evgeny Krylov, US Provisional Application Number 60/310,902, filed 8/8/2001; Attorney Docket M018, entitled Radio Frequency Capacitive Discharge Ionizer For Analyzer, by Raanan A. Miller and Erkinjon G. Nazarov, US Provisional Application Serial Number 60/335,219, filed 10/25/2001; and Attorney Docket M031R, entitled Radio Frequency Capacitive Discharge Ionizer For Analyzer, by Raanan A. Miller, Erkinjon G. Nazarov, and Evgeny Krylov, US Provisional Application Serial Number 60/340815, filed 12/12/2001, all incorporated herein by reference.

BRIEF DESCRIPTION OF THE DRAWINGS:

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of preferred embodiments of the invention, as illustrated in the accompanying drawings in which like reference characters refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the invention.

Figure 1A is a generalized block diagram of apparatus employing a capacitive discharge plasma ionizer in practice of the invention.

Figure 1B is an illustrative resonant RF drive circuit of the capacitive discharge plasma ionizer in practice of the invention.

Figures 1C and 1D show alternative waveforms supplied by an RF drive circuit of the invention.

Figure 1E shows an alternative embodiment of the invention where (1) positive and negative FAIMS spectra which can be generated by a capacitive discharge plasma ionization source of the invention with both electrodes insulated compared to (2) positive and negative spectra generated with a radioactive source.

Figure 1F compares (1) the FAIMS spectra of Figure 1E(2) for a radioactive source to (2) positive and negative spectra generated in practice a capacitive discharge plasma ionization source of the invention with only one electrode insulated.

Figure 1G is a comparison of the mass positive spectra (1) from a radioactive source and (2) from an embodiment of the invention, detected by a mass spectrometer with a low plenum gas flow.

Figure 1H shows negative mode mass spectrometer spectra for (1) pure air, and (2) pure air plus 20ppm of SF_6 (M=146), after plasma ionization in practice of the invention.

Figure 1I shows FAIMS detection of mercaptan and purified air ionized in an embodiment of the capacitive gas discharge plasma ionizer of the invention.

Figure 1J shows mass spectra for acetone generated and reproduced by ionization of acetone in practice of the invention.

Figure 2A shows an embodiment of a capacitive discharge plasma ionizer structure according to the present invention.

Figures 2B-2D are alternative embodiments of the capacitive discharge structure of the invention.

Figure 3 is a planar embodiment of the capacitive discharge structure of the invention.

Figure 4 is a needle electrode embodiment of the capacitive discharge structure of the invention.

Figure 5-6 Omit.

Figures 7-10 depict embodiments of the capacitive discharge plasma ionizer in

practice of the invention.

Figures 11 and 12 are schematics of alternative embodiments of capacitive discharge plasma ionizer of the invention with an accelerator electrode.

Figures 13A-C are alternative accelerator electrodes of the embodiments of Figures 11 and 12.

Figures 14A-D are schematics of alternative configurations of a planar high field asymmetric waveform ion mobility spectrometer incorporating an ionization device in practice of the invention.

Figures 15A is an end view of a spectrometer apparatus with plasma ionization devices in practice of the invention.

Figures 15B is an end view of a spectrometer apparatus with four electrodes arranged with each electrode positioned orthogonally to an adjacent electrode in practice of an alternative plasma ionization device of the invention.

Figure 16 is a system of the invention incorporating a capacitive discharge plasma ionization source for ionizing compounds in a chemical sample and having a FAIMS analyzer for receipt, analysis and identification of the ionized compounds.

Figure 17A shows intermeshed electrodes of a plasma generator formed on a single substrate in practice of the invention, and Figure 17B shows an alternative embodiment rotated 90 degrees on the surface of the substrate.

Figure 17C is a microchip device with opposed substrates having a plurality of electrodes for plasma ionization and analysis according to the invention.

DETAILED DESCRIPTION OF THE INVENTION:

Figure 1A is a generalized block diagram of a system 10 in practice of the invention used to analyze the composition of chemical compounds in a gas sample S. The system 10 includes a capacitive discharge plasma ionization source 11 and a detector 20. The detector may be a mass spectrometer (MS), ion mobility spectrometer (IMS), high-field asymmetric waveform ion mobility spectrometer (FAIMS), time-of flight spectrometer (TOF) , or the like. In this embodiment, the capacitive discharge plasma ionization source 11 is separate from but in communication with spectrometer 20. Alternatively, the source 11 may be integrated into the spectrometer to form an integrated system 10.

Capacitive discharge plasma ionization source 11 includes a pair of electrodes 14, 16, which are preferably isolated, or insulated, as further described below. When a sufficient voltage is supplied across electrodes 14, 16, a discharge field F is established. Now the gas is flowed into the field in the gap G between the electrodes; the gas is thus ionized by capacitive discharge between the electrodes. This discharge ionization produces a plasma 40 from the air, with both positive and negative ions, such as shown in Figure 1G(2) and Figure 1H(1), usually including $(H20)_n$, H^+, O^-, O_2^-, O_3^-, $(N_xO_n)^+$, and $(N_xO_y)^-(H_2O)_n$.

In operation, a gas and sample S feeds through inlet 13 into ionization region 36. The gas again is ionized by the discharge in the RF field F between the electrodes forming the plasma ions. The plasma in turn ionizes the sample S and forms ions M^+, MH^+, and M^-. All of the generated ions now present in the ionization region 36 exit through an outlet passage 37 for further utilization. In an analytical embodiment of the invention, these ions now proceed from passage 37 into spectrometer 20 for analysis.

A preferred control and drive circuit 22 of the invention is shown in Figure 1A and in more detail in Figure 1B, including a pulse generator 22a, a resonance generator 22b, and a resonant circuit 22c. The resonant circuit 22c includes electrodes 14, 16 spaced by gap G) and inductor L. As will be appreciated by a person skilled in the art, a microchip or other logic or controller device 22d may also be supplied in communication with the drive circuit 22, and also possibly having inputs from other system feedback or data sources, to affect total system control.

We have found that use of the resonant drive 22 to produce a high frequency (RF) high voltage increases discharge stability and decreases power consumption. In a preferred embodiment, the resonant drive circuit 22 also provides system stability via negative feedback. More particularly, it will be appreciated that plasma pumping energy strongly depends on field strength. If applied voltage (and electric field correspondingly) rises, then discharge energy increases. This results in increasing rate of ionization and consequently increase in discharge conductivity. Unchecked, this increase could result in a excessive increase in plasma energy and heating.

However, if we form the electrodes 14, 16 as a capacitor in L-C resonant circuit 22c, then stability can be obtained. If the capacitor's conductivity increases, then the Q-factor of the resonant circuit decreases. Since applied voltage is proportional to the Q-factor, the voltage decreases as well. Thus electrodes 14, 16 are part of a negative feedback loop to maintain the plasma at a desired energy level for a given drive voltage and frequency, preventing runaway plasma growth and overheating.

A particular drive circuit 22 design will depend on target plasma levels, electrode and gap dimensions, among other things, as will be appreciated by a person skilled in the art. Nevertheless, typically a high-frequency voltage, with an amplitude of several hundred volts, is required to initiate and maintain the discharge in atmospheric conditions. The reactive power in the megahertz frequency range will be tens of watts for a capacitive load of tens of picofarad. Therefore the present invention preferably employs a resonant oscillator with a capacitive load as a component of the output LC-circuit, as will be further appreciated by a person skilled in the art.

In practice of the invention, the electric field has an RF component that may be of a standard or custom shape (e.g., sinusoidal, bias offset, pulse width modulated, or otherwise). For example, embodiments of the invention are operable with a sinusoidal high frequency high voltage waveform applied to electrodes 14, 16, as shown in Figure 1C. Preferably further efficiency is achieved by using a pulsed ("packet") waveform, as shown in Figure 1D.

Use of the packet waveform increases discharge stability, decreases power consumption, and further controls ionization efficiency. More specifically, the pulsed design

follows from the recognition that a finite time interval is required for the plasma instability to reach the macrolevel. Therefore, energy is delivered to the discharge gap by short high frequency (RF) high voltage high intensity pulses, so that the instability does not have the time to develop. A dense plasma is formed in this case, since the ionization strongly depends on the energy. Once a pulse is switched off, dissipative processes suppress the development of the instability. If the pulse repetition period is comparable to the energy relaxation time in the plasma, its period-averaged parameters, including the degree of ionization, will be quasi stable. In one illustrative embodiment, the pulse had a frequency of about 1-20 MHz, a duration of about 1 msec, and a peak-to-peak voltage of about 1000 – 10000 volts. The duty cycle (t_1/t_2) of the packet waveform was approximately 1/11.

In any event, use of the packet waveform is beneficial. Because the efficiency of ionization of the plasma ionization device 11 is directly proportional to the voltage supply duty cycle, drive circuit 22 consumes less power (proportional to duty cycle) to provide the pulsed waveform versus the continuous waveform. Further, the service lifetime of the ionization device 11 increases by a factor of 5 to 10 time when the ionization device is powered with a pulsed packet waveform.

With either continuous or packet waveform, a sufficient RF voltage will be developed across electrodes 14, 16 to cause the local gas to electrically discharge and form a plasma. Figures 1E and 1F show positive and negative spectra produced in clean laboratory air at atmospheric pressure, detected using a FAIMS spectrometer.

Figure 1E(1) shows positive and negative spectra which could be generated in an alternative embodiment of the invention by a capacitive discharge plasma ionization with both electrodes, 14, 16 being insulated, compared to (2) positive and negative spectra generated with a radioactive ionization source (^{63}Ni at 10mCu). It is clearly shown in Figure 1E that a non-radioactive ionization source of the invention (Figure 1E(1)) could be substituted for a radioactive source (Figure 1E(2)) to provide essentially the same performance.

In Figure 1F, a comparison was made between the same radioactive source of Figure 1F(1) against an embodiment of the invention with only one of electrodes 14, 16 being insulated. Nevertheless, the positive spectra are nearly identical between the ^{63}Ni source of

Figure 1F(1) and the embodiment of the invention of Figure 1F(2).

Discussion of the benefits of isolated electrodes will be discussed below, however we note here that the negative spectra in Figure 1F(2) was somewhat degraded versus that of Figure 1F(1). Yet the negative spectra still retain adequate information to be useful. For example, the species indicated by peak p1 in the negative spectra of Figure 1F(1) is clearly discerned as peak p2 in the negative spectra of Figure 1F(2).

In addition to the foregoing, we have found that the plasma source of the invention is capable of providing adequate ionization energy in many applications, operating on as low as only a few watts (e.g., two watts in one embodiment). Furthermore, in comparison of Figures 1E and 1F, the beta source was capable of generating a maximum ion current of 4p, while the invention delivered a maximum 12 pA. Therefore, it is evident that a clean, efficient and powerful plasma ionization source can be provided in practice of the invention.

We have clearly demonstrated the utility of the present invention as a viable substitute for a radioactive plasma source. More specifically, Figure 1G is a comparison of the positive spectra (1) from a radioactive source and (2) from an embodiment of the invention, detected by a mass spectrometer with a low plenum gas flow (i.e., a barrier counter-flow of clean gas to prevent introduction of laboratory air into the MS). Frame (1) shows background mass spectra for ^{63}Ni in an apparatus that generated 4,000 ions per second. Frame (2) is an embodiment of the invention that recreated the same or comparable spectra and yet with an ion production rate of 50,000 ions per second. It is therefore clear that the present invention is a rich source of ions for a broad range of applications. (It is further noted that while Figure 1G shows MS results with a low plenum gas flow, the present invention is not limited to particular flow rates, whether in the plasma ionizer (sample and carrier gas) or in a FAIMS analyzer (ion flow) or at the front end of an MS (plenum).)

Figure 1H shows negative mode mass spectrometer spectra for (1) pure air, and (2) pure air plus 20ppm of SF_6, after plasma ionization in practice of the invention. Quite clearly, comparing the two frames, the SF_6 (M=146 amu) peak stands out and is clearly identified, while the background spectra retains its integrity.

Exceptional detection results may also be obtained using other detection devices. For example, in Figure 1I a FAIMS (also known as RFIMS) spectrometer received an ionized output of a mercaptan sample and purified air as outputted by an embodiment of the capacitive gas discharge plasma generator of the invention. The negative and positive mercaptan (+/-mer.) peaks and background spectra are clearly defined.

It is thus clear that the plasma generator of the invention is a useful and versatile non-radioactive plasma ionization source for a variety of applications. Further evidence of this utility, by way of additional illustration, is shown in Figure 1J, where the mass spectra for acetone was generated and reproduced by ionization of acetone in practice of soft ionization within the invention. It will be understood that in practice of embodiments of the invention, this mass spectra can be used for the identification of acetone. Thus the simplicity and utility of the invention should now be appreciated as being quite broad.

Isolation of the electrodes 14, 16 from the plasma environment has beneficial effects. Therefore in embodiments of the invention, one or both electrodes are isolated. Preferably both electrodes are isolated, however, it is less common but possible where an embodiment of the invention could be used without any isolation of the electrodes. This might occur where stability is the primary motivation, for example.

Nevertheless, in a preferred embodiment of the invention, both electrodes 14, 16 are isolated, such as by use of insulating material. The insulator is used to separate the gas sample being ionized from the surfaces of the electrodes that are used to generate the plasma field F between the electrodes.

The insulator is preferably a dielectric material. A dielectric is a substance that is a poor conductor of electricity but an efficient supporter of an electrostatic field. Examples of dielectric materials include porcelain (ceramic), mica, glass, plastics, the oxides of various metals, and some liquids and gases, all of which may be employed as insulators on, around or

in between electrodes 14, 16 in embodiments of the present invention.

A dielectric material serves two functions. First, its presence traps charges from the plasma, reducing the average potential of the plasma relative to the electrodes. This is important since the potential difference between the electrodes and the plasma defines how much ion bombardment of the electrode surface or dielectric takes place (and consequently decreases etching of the electrodes). The higher the potential difference, the more bombardment. This ion bombardment is unwanted since it leads to formation of ions from the electrode material in the sample plasma and contaminates the sample spectra. Second, the dielectric material tends to be inert so that reactive gases can be ionized without interaction with the electrodes. The resulting is a clean plasma ionization environment.

Furthermore, in one embodiment, a glass or crystal tube encloses the ionization region, including enclosing the resulting plasma (and disassociated electrons) within the electric field between the electrodes. Sample and carrier gas is flowed into this environment for ionization. In yet another embodiment, the electrodes are formed on the outside of an insulated structure that forms an insulated flow channel and the plasma is generated within the insulated channel between the insulated electrodes.

While these and other embodiments of the invention may now occur to a person skilled in the art, we disclose further embodiments of the invention by way of illustration and not by way of limitation. These and yet other variations are nevertheless within the spirit and scope of the present invention.

For example, referring to Figure 2A, apparatus 10 includes a plasma ionization device 11 positioned within a flow channel 12. The ionization device 11 defines an ionization region 36 about the ionization device 11. Channel 12 has a planar geometry formed by an upper and a lower flat substrate 24, 26 or alternatively, the ionization device 11 can be placed within a cylindrical channel, Figure 2B.

The ionization device 11 of Figure 2A includes a first electrode 14 placed within an insulating capillary tube 18 and a second electrode 16 wrapped around the capillary tube 18. The electrodes are separated by a gap G. One end of each of electrodes 14 and 16 is

connected to the RF drive voltage supply 22 such that the electrodes function as the plates of a capacitor, separated by gap G, with the drive RF voltage applied across the two electrodes.

In a further embodiment of the invention, as shown in Figure 2B, ionization device 11 includes an insulated substrate, such as glass capillary tube 18, coated with a metallization layer 23; this layer is parted at "x" to define two metallization regions forming electrodes 14', 16' of a plasma generator of the invention. The inner faces 14", 16" of these electrodes are formed on the insulating surfaces of the tube 18 and face each other through the tube 18 and across the open center 18c of the tube 18. It will be understood that an RF signal from source 22 is applied to these electrodes to generate field F within the tube 18.

In this embodiment, the gap separating the electrodes is defined by the diameter of the tube 18. Within the tube 18, the entire open center 18c may be utilized as an ionization region. In operation, the gas and sample S are flowed into the central passage 18c of the tube 18 through inlet 13. The carrier gas is ionized and forms a plasma field F which in turn ionizes the sample S between the electrodes 14, 16. Since the plasma has both positive and negative ions, the sample may be ionized into both positive and negative ions. The ions subsequently exit through outlet 15 for further use, such as in an ion mobility spectrometer.

In illustrative embodiments, such as shown in Figures 2A and 2B, the channel 12 has a diameter, d_1, of about 0.001 – .002 inches. The capillary tube 18 as a length, 1_1, of about 0.01-.05 inch, a diameter, d_2, of about 0.001-0.1 inches. The capillary tube 18 is made of quartz, glass or of any other suitable dielectric material. Electrodes 14 and 16 are typically made of gold, platinum, chromium, or any other suitable chemically passive conductive material.

In further embodiments of the invention shown in Figures 2C and 2D, conducting electrodes 82, 84 are placed into tube-like dielectric sheaths 86, 88 (of glass, quartz, ceramic or other suitable material). Preferably these sheaths are fixtured so that the separation between the electrodes is fixed within ionization region 36. This separation can range from having the dielectric sheaths touching to having a separation of 5 mm or more.

It will be further observed that the electrodes 82, 84 in the embodiment of Figure 2D

are held and joined via collars 92, 94. Just beyond collar 94, the ionization region is effectively terminated as the electrodes being to diverge. This arrangement enables defining the length of ionization region and thus avails predictable performance characteristics. Additionally, abutting collars 96, 98 are affixed on each of the tubes 86, 88 after collar 94 to fix this divergence. In various embodiments, the electrodes may be formed of conventional thin wire filaments and may be contained in a tube or coated with a dielectric or other insulating material.

The electrodes are separated by gap G, whether they are embedded in a dielectric material and mated or are within insulating tubes which abut. As will be appreciated by a person skilled in the art, the electrode diameter and dielectric coating material type and diameter are selected such that the fields generated between the electrodes are accessible to the gas flow. Figure 2C is a simplified example, wherein the gas flows between the electrodes and therefore through the plasma-generating field between the electrodes. Figure 2D is more difficult, wherein the air flows along the perimeter of the tubes and the field generated between the electrodes must extend into this peripheral flow. Therefore the applied signal, the filament and coating diameter all must be accommodate this external peripheral field F.

Figure 3 is an alternative embodiment of the capacitive discharge structure of the invention, wherein ionization device 11 is configured as a planar apparatus 10. The first electrode 14 is a planar electrode on the underside of a first substrate 24, and the second electrode 16, also a planer electrode, is on top of a second substrate 26. The first electrode 14 and the second electrode 16 are connected via a pair of leads 28a, 28b to the same voltage supply 22, with respective conductive terminal pads 30 and 32.

In further practice of the embodiment of Figure 3, an insulation layer 34 made of, for example, Al_2O_3 (Alumina) or SiO_2, or the like, is formed over one or both of electrodes 14, 16. In the embodiment shown in Figure 3, the ionization device 11 is arranged with the opposing surfaces of the inner insulators 34 being spaced apart by a distance of d_3, of about 100 mm, defining gap G as ionization region 36. Furthermore, in the embodiment of the invention shown in Figure 4, a needle electrode 170 is coated with insulator 172, and

cooperates with a planar electrode 174 to form the plasma generator of the invention. Alternatively, the planar electrode 174 may be replaced with a second needle electrode.

It will be appreciated that although electrodes 14 and 16 are positioned parallel to each other in the device shown in Figure 3, such a configuration is not necessary for the ionization device 10 to operate. Accordingly, the electrodes may be parallel or angled, flat or curved, within embodiments of the invention.

In Figure 7, electrodes 14, 16 are positioned at an angle so that the ionization region has a narrow region and a wide region. Electrodes 14, 16 are formed respectively on upper and lower substrates 24, 26, which are positioned at an angle, α. The angle, α, may be from about 10 degrees to about 90 degrees so that the ionization region 36 has a narrow region 41a and a wide region 41b. The gas that enters the ionization region is first ionized in the narrow region because the electrodes are closer together, which creates a higher field strength and hence a more intense ionization field. The electric field dissipates from the narrow region to the wide region the ionization process propagates from the narrow region to the wide region to generate the plasma (++,--). Ionization of the sample now proceeds as earlier described.

Up to now the planar electrodes 14 and 16 (Figures 3 and 7) have been shown with a respective inner insulator 34 that covers each of the electrodes. However, the plasma ionization device 11 of the invention is capable of functioning without the use of the inner insulator 34 on both electrodes. For example, in an alternative embodiment shown in Figure 8, the second electrode 16 is not covered by an insulating material. Furthermore, the first electrode 14 need not be covered by the insulator. That is, both electrodes 14, 16 may be exposed directly to the sample gas.

Alternatively, as shown in Figure 9, electrodes 14 and 16 can be mounted to the respective outer surfaces of the substrates 24, 26. As evident in Figure 9, neither electrode is covered by an insulating material. In yet another alternative embodiment illustrated in Figure 10, electrode 16 is mounted to substrate 26, and electrode 14 is made of a dielectric substrate 50 coated with a metal layer 52a on one side of the dielectric substrate 50. The opposite side of the dielectric substrate 50 can also be coated with an additional metal layer 52b. In either

case, electrode 14 is brazed to substrate 24 or attached with any other suitable attachment mechanism, such as, for example, epoxy glue.

Referring now to Figure 11, an alternative embodiment of the ionization device 10 includes an accelerator electrode 60, having its own self potential, mounted to the insulator layer 34 which covers electrode 14. Alternatively, electrode 14 and the accelerator electrode 60 can be mounted on opposite sides of substrate 24 as depicted in Figure 12.

In either of the just described embodiments, the accelerator electrode 60 can be a series of small electrodes 62 interconnected with conductive wires 64, Figure 13A, or a mesh of interconnected horizontal 66 and vertical 68 wires, for example, as shown in Figure 13B. Alternatively, as shown in Figure 13C, the accelerator electrode 60 can be an ensemble of small conductive electrodes 61 that are surrounded by a ring of conductive material 63, such as, for example, certain metals.

The various embodiments of the ionization device 11 discussed above are quite suitable for use in many types of gas analyzers and detectors. For example, there is shown in Figure 14A a planar high field asymmetric waveform ion mobility spectrometer apparatus 70 which uses the ionization device 11 to generate ions for the chemical analysis of the sample S in the carrier gas CG.

The apparatus 70 includes the ionization source 10, a filter 72 defining a filter region 74 between filter electrodes 76, 78, and a detector 80 defining a detection region 82 between detector electrodes 84, 86. Asymmetric field and compensation bias are applied to the filter electrodes 76, 78 by a drive circuit 88 within a control unit 90. The detector electrodes 84, 86 are also under the direction of the drive circuit 88 and control unit 90.

Briefly, in operation, the carrier gas, CG, is ionized in plasma region 36 forming plasma ions ++,--, and the sample S in turn is ionized creating both positive and negative ionized molecules, M^+ and M^-. Based on FAIMS ion filtering techniques, only certain ion species pass through the filter region 74 while others are filtered out. Those that pass through are detected at detector electrodes 84, 86. Preferred configuration of apparatus 70 and its

operation is described in greater detail in U.S. Patent Application No. 09/358,312, filed July 21, 1999, the contents of which are incorporated herein by reference.

As depicted in Figure 14A, electrodes 14, 76 and 84 are coplanar and electrodes 16, 78 and 86 are coplanar. Alternatively, as shown in Figure 14B, apparatus 70 includes a necked down region 99 in which the ionization device 11 and electrodes 14, 16, resides. In this configuration, electrodes 14, 16 are spaced apart by a distance, d_4, of about 100 μm, while there is a distance, d_5, between the filter electrodes 76, 78.

In yet another embodiment shown in Figure 14C, the ionization device 11 is located within a channel 101 defined as outside a pair of substrates 100, 102. In such an arrangement, the carrier gas, CG, splits, and partly flows within the ionization region where it is ionized to form the plasma, ++,--, and also over the outside of the ionization device 11 enclosed within the outer substrates 100, 102. The sample S then flows into the plasma ions ++,-- within the ionization region 36 and is ionized. The carrier gas now carries the ions from the outlet 15 of the ionization device 11 to the filter region 74 of the filter 72 for further analysis.

Referring now to Figure 14D, there is shown another alternative embodiment of apparatus 70 that includes a sample source 71 which is separate from the ionization device 11. A gas, CG, is ionized to create ions, ++,--, which in turn interact with and ionize sample S, before they flow into the filter region 74. With such a configuration, a variety of gases which are different from the sample gas can be mixed to create the ions.

In further embodiments the electrodes 14, 16 are positioned to create an intense ionization region, as an improvement of the embodiment of Figure 7. For example, in the embodiment shown in Figure 15A, a pair of ionization devices 11, 11 with non-parallel electrodes are employed in apparatus 70. The ionization devices 11, 11 are positioned within a channel 110 defined by an upper substrate 100, a lower substrate 102, a first spacer plate 104, and a second spacer plate 106, of plasma ionization apparatus 70. As the sample enters the ionization region 36, the ionization process initiates in the narrow regions 40 nearer each spacer plate and then progresses towards the wider regions 42 nearer the center of the channel 110.

These intense ionization regions can also be formed with the device illustrated in Figure 15B which is conceptually an extension of the embodiment shown in Figure 15A. Referring to Figure 15B, the ionization device 11 includes a first electrode 114 mounted to an upper substrate 100, and a second electrode 116 mounted to an inner surface of a lower substrate 102. In addition, there is a third electrode 118 and a fourth electrode 120 mounted to the inner surfaces of side spacer substrates, 104, 106, respectively.

The electrodes 114, 116, 118, and 120 are coupled to a voltage source 22 (not shown) and are arranged with electrodes 114 and 118 forming the plates of one capacitor, and the electrodes 116 and 120 forming the plates of another capacitor, consistent with the invention. The electrodes 114 and 116 are of the same polarity, while the electrodes 116 and 120 are of the opposite polarity. With this configuration, there are four intense ionization regions 140, 142, 144, and 146 near the corners of the electrodes. When the gas enters the ionization region 36, the ionization process begins at these intense ionization regions and then propagates towards the center 150 of the ionization region 36 to form the desired plasma.

Figure 16 shows an alternative embodiment of the invention, wherein capacitive discharge ionization source 11 is integrated with a FAIMS apparatus in analytical system 10. The ionization device 11 is depicted with electrodes 14, 16 that produces the plasma of positively and negatively charged ions from high energy electric field F between the electrodes. In this embodiment, at least one and preferably two of the electrodes 14, 16 is coated with dielectric D. In alternative embodiments, the dielectric is mechanically distinct from the electrodes 14, 16, as opposed to a coating.

Continuing to refer to Figure 16, system 10 further includes FAIMS apparatus 240, having filter 250 and detector 260 formed on substrates 238, 239. Filter 250 applies a compensated high field asymmetric waveform to a pair of filter electrodes 252, 254 that generate a high electric field therebetween. According to ion mobility characteristics of the ions passed into the filter field, a species of ions is passed for detection to a detector 260 which has a pair of detector electrodes 262, 264. In a typical FAIMS manner, the detection event is correlated with the applied drive voltages and known device performances to characterize the detected ion species, and now this can also be correlated with drive and

control of the ionization device 11, for total analytical system control.

In operation, the carrier gas with a sample of chemical compounds are inputted at inlet 265 and the gas flows through the apparatus and out exhaust 266. Gas flow rate and pressure may also be controlled by use, for example, of a pump 268 associated with exhaust 266. The FAIMS system is driven and controlled by controller and driver circuit 222, which may be incorporated into and packaged with the plasma controller and drive circuit 22. Furthermore, the plasma generating electrodes 14, 16, filter electrodes 252, 254, and detector electrodes 262, 264 may all be separate and distinct structures or may be formed as electrodes on the surfaces of substrates, 238, 239, for example. The plasma-generating can be controlled and provides adequate energy to ionize compounds.

In the embodiment of Figure 14C, the efficiency of ionization of the sample is increased by reducing the amount of carrier gas in the ionization region. In an alternative embodiment of the invention, also shown in Figure 16, in order to increase the ratio of sample S to carrier gas, and thus to increase the efficiency of ionization of the sample, sample S is introduced with a minimized amount of carrier gas into ionization region. The carrier gas is ionized to form the plasma, which in turn ionizes the sample S, and then a second stream of carrier gas CG is introduced via an additional inlet 241 to carry the ions on for further analysis. Now a lower amount of background gas is ionized which relatively increases the ratio of sample to gas, thus improving ionization efficiency and reducing the RIP in the analyzer.

Turning now to Figure 17A, electrodes 14, 16 are formed on a single substrate 24'. The electrodes each extend to define a number of tines, such as tines 14a, 14b, 14c, 16a, 16b. These tines enable the electrodes to be intermeshed while forming plasma generator 11. Electrodes 14, 16 are driven by the RF source 22. Figure 17B is similar but with the tine orientation rotated ninety degrees.

It will be appreciated that in a preferred embodiment, these electrodes are isolated from the gas flow. Such isolation is by use of an isolating or insulating layer, for example a dielectric coating 34 preferably formed on each exposed electrode (and tine) surface, such as, for example, Al_2O_3 (Alumina) or SiO_2, or the like, as indicated in Figure 17B in dotted

outline. (It will be further appreciated that various embodiments of the invention include use of isolation as earlier discussed and as shown in Figure 17B and that this isolation is not shown in Figures 17A and 17C merely in order to ease presentation.)

The single substrate 24' may be enclosed in a flow channel 12 defined by a housing H to provide an entire plasma generator 11 of the invention, with sample intake at inlet 265 and exhaust at outlet 266.

The plasma generator 11 of the invention may be formed on the same substrates that incorporate a FAIMS device. As shown in Figure 17C, microchip 290 is formed incorporating a plasma generator 11 of the invention with identical or mating opposed substrates, 224, 226. In various embodiments, a separate plasma generator as in Figure 17A may be formed on each of the facing substrate or one plasma generator may be formed by the opposed substrates, as in Figure 16. A FAIMS device 240, having a filter 250 and optionally a detector 260 may also be defined within the same microchip structure 290.

Formation of a FAIMS device on mating substrates is disclosed in copending application serial number 09/882,883, filed 6/15/2001, entitled SPECTROMETER CHIP ASSEMBLY, incorporated herein by reference. Elongation of the leading or front end of such spectrometer chip assembly would accommodate formation of plasma generator 11 therein, such as now shown within microchip 290 in Figure 17C.

In practice of embodiments of the invention, separation of the substrates and accurate spacing of the electrodes is desirable and may be achieved as needed, such as by use of spacer parts 292, 294 in the microchip structure 290, Figure 17C. The substrates 224, 226 are formed mated against spacers 292, 294, which may be integral extensions of the substrates, or a housing, or separate components, as needed.

In the analytical system 10 shown in Figure 17C, the carrier gas and sample S is introduced at inlet 265, and is ionized by the plasma process at generator 11. The ionized particles are analyzed in FAIMS device 240 (via FAIMS filter 250). The filter output may be directed to the input of a mass spectrometer or other detector device or simply to the input of an onboard detector 260, as shown, and then is exhausted at exit 266.

It will now be appreciated that the present invention relates to a novel, low-cost, non-radioactive, highly-efficient, clean and stable, radio frequency plasma ion source. It is capable of providing a wide range of plasma levels and is operable a low power over a range of pressures, including atmospheric pressure, in air. The invention is capable of ionizing a wide range of compounds, ranging from those having low ionization potential (such as acetone) to those having high ionization potential (such as SF_6), among various other compounds, for example.

It will be appreciated by a person skilled in the art that the present invention can be operated with control over formation of ions and ion species. As an illustration, the amount of energy in the plasma can be controlled, such as by control of the energy supplied by drive circuit 22. It will be appreciated that control of the amount of energy imparted into the gas and the resulting plasma controls the ion species generated in the plasma. By controlling this energy we can control formation of ions. Furthermore, this control may also be exercised to prevent formation of unwanted ions, such as nitrogen ions (NOx species), which can interfere with detection of other negative ions. It will be further appreciated by as person skilled in the art that adjusting gas flow rate can also be used to control the ion species that are formed in the plasma.

Based upon the foregoing discussion and illustrations, it will now be appreciated that plasma sources of the invention are useful in a wide range of systems that require sample ionization. The invention may be provided as a stand-alone device or may be incorporated into a larger system that can benefit from a clean and stable source of ions. Examples of such systems include FAIMS, ion mobility spectrometers, and atmospheric chemical pressure ionization spectrometers, among others. In fact, the present innovation has many practical applications, too numerous to illustrate herein.

It will now be appreciated that this invention has been particularly shown and described with reference to illustrative and preferred embodiments thereof. It will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit scope of the invention.

CLAIMS

What is claimed is:

1. A plasma ionization source for generating, comprising:

a capacitive discharge device having at least two electrodes, said electrodes being spaced by a gap,

means for generating RF signals, said signals applied to said electrodes for generating a field associated with said gap, and

means for applying a gas to said field, said gas being ionizing by said field and generating a plasma of ions associated with said gap,

means for minimizing contact of said ions with at least part of at least one of said electrodes, and

means for transport of said ions out of said gap for further use.

2. The source of claim 1 further including means for enabling generation of said plasma at a pressure including at or about atmospheric pressure in air.

3. The source of claim 1 wherein said means for generating further includes a resonant wherein said electrodes are part of said resonant circuit.

4. The source of claim 3 wherein said means for generating includes a circuit for stabilizing said plasma temperature.

5. The source of claim 3 wherein said means for generating includes a negative feedback circuit for stabilizing said plasma current.

6. The source of claim 3 wherein said resonant circuit includes said negative feedback circuit and said electrodes.

7. The source of claim 3 further comprising means for generating a packet waveform to drive said electrodes for generation of said plasma.

8. The source of claim 1 further including means for transport of said gas in said device, further including an inlet for receipt of said gas and an outlet for flow of said ions for downstream use, said ions being transported from said gap to said outlet by said transport means.

9. The source of claim 1 wherein said means for minimizing includes insulation on at least one of the electrodes for preventing said plasma from contacting said at least one electrode.

10 10 The source of claim 9 wherein said electrodes are insulated from contact with said ions.

11. The source of claim 10 wherein said insulation is a dielectric material.

12. System with efficient plasma ionization, comprising:

a capacitive discharge device for receipt of a gas and for generating a plasma of ions from said gas,

said device including at least a pair of electrodes, said electrodes providing an electric field therebetween and through which at least a portion of said gas passes, said gas being ionized by said field to form said plasma, and

means for stabilizing said plasma.

13. System of claim 12 wherein said means for stabilizing includes a negative feedback circuit to regulate said field to control efficiency of said plasma generation.

14. System of claim 12 wherein said electrodes form plates of a capacitor, further comprising a resonant circuit coupled to said plates for generating said plasma.

15. System of claim 14 wherein said electrodes are part of said resonant circuit.

16. System of claim 14 wherein said means for stabilizing includes said resonant circuit and said capacitor, said resonant circuit applying an RF voltage to said electrodes.

17. System of claim 12 wherein said means for stabilizing includes a circuit for stabilizing said plasma temperature.

18. System of claim 14 wherein said resonant circuit includes a circuit for generating a packet waveform to drive said electrodes for generation of said plasma. .

19. System of claim 12 wherein said means for stabilizing includes isolation means for isolating at least one surface of at least one electrode from said plasma.

20. System of claim 19 wherein said means for stabilizing includes isolation means for isolating surfaces of said electrodes from contact with said plasma.

21. System of claim 19 wherein said isolation means includes an insulating medium associated with at least one of said electrodes.

22. System of claim 21 wherein said medium includes an insulator material.

23. System of claim 21 wherein said medium includes a dielectric material.

24. System of claim 12 further including means for enabling formation of said plasma at a pressure including at or about atmospheric pressure in air.

25. System of claim 12 wherein said means for stabilizing said plasma includes an isolation part to separate said plasma from at least one of said electrodes.

26. System of claim 12 wherein at least one electrode is curved, flat, molded, pointed, or a wire.

27. System of claim 12 further comprising means for generating positive and negative ions simultaneously in said plasma.

28. System of claim 12, further comprising a spectrometer and means for receiving a sample for ionization in said plasma, and further including means for delivering said ionized sample out of said gap to the input of said spectrometer.

29. System of claim 18, wherein said spectrometer evaluates ions based on ion mobility.

30. The source of claim 1 further comprising means for generating positive and negative ions simultaneously in said plasma.

31. The source of claim 1, further comprising a spectrometer and means for receiving a sample for ionization in said plasma, and further including means for delivering said ionized sample out of said gap to the input of said spectrometer.

32. The source of claim 1, wherein said spectrometer evaluates ions based on ion mobility.

33. Apparatus for plasma ionization, comprising:

a capacitive discharge means for receipt of a gas and for generating a plasma of ions from said gas,

said device including at least a pair of electrodes separated by a gap, said electrodes providing an electric field in said gap and through which at least a portion of said gas passes, said gas being ionized by said field to form said plasma in said gap, and

a device for stabilizing said plasma in said gap.

34. Apparatus of claim 33 wherein said stabilizing device is a material barrier associated with at least one of said electrodes.

35. Apparatus of claim 33 wherein said electrodes are separate by a gap and said stabilizing device is a resonant circuit which controls the temperature of the plasma in said gap.

36. Apparatus of claim 33, further comprising a capillary tube, first and second electrodes being associated with the surface of the capillary tube, the sample flowing within the tube.

37. Apparatus of claim 33, wherein said electrodes are planar electrodes mounted to associated substrates, the substrates being insulators and mounted together to form a flow channel for flow of the plasma therein.

38. Apparatus of claim 33 The device of claim 34, wherein said material barrier further comprises an insulating layer covering at least one of said electrodes.

39. Apparatus of claim 38, wherein at least one of said electrodes is mounted to a surface of a substrate.

40. Apparatus of claim 33, further comprising a capillary tube, a first of the electrodes being a wire positioned within the tube and along the length of the tube, and a second of the electrodes being a second wire wrapped around the tube.

41. Apparatus of claim 33, further comprising a pair of capillary tubes, a first of the electrodes being a wire positioned within one said tube and along the length of said tube, and a second of the electrodes being a second wire, said second wire running in said second tube, said wires forming said electrodes and further comprising a collar for joining said tubes and forming said gap between said electrodes.

42. Apparatus of claim 33 wherein said electrodes are formed as wire filaments contained in a dielectric.

43. Apparatus of claim 42 wherein the dielectric forms a tube on each of said electrodes.

44. Apparatus of claim 43 further comprising abutting collars affixed on each of said tubes, said abutting collars holding in juxtaposition.

45. Apparatus of claim 33 wherein one said electrode is a needle electrode.

46. Apparatus of claim 33 wherein at least one said electrode is a planar electrode.

47. Apparatus of claim 33 further including a sample introduction part for introducing at least one chemical sample molecule into said plasma, said plasma ionizing said at least one molecule.

48. Apparatus of claim 47 further comprising a detector, wherein said ionized molecule is passed to said detector for analysis and detection.

49. Apparatus of claim 48 further comprising substrates associated with a housing and forming a flow channel, said capacitive discharge means and said detector cooperating within said housing and said ionized molecule passing from capacitive discharge means to said detector via said flow channel.

50. Apparatus for producing capacitive discharge plasma, comprising:

a microchip package having a pair of substrates and forming a housing, said substrates associated with said housing and forming a flow channel, and

a plasma generator formed on said substrates, said generator for generating an electric field through which at least a portion of a supply passes, the field ionizing the supply and forming a plasma of ions, said generator including at least two electrodes facing each other on said substrates and separated by a gap, said field formed associated with said gap, and

a sample introduction part associated with said flow channel for introducing at least one chemical sample molecule into said plasma, said plasma ionizing said at least one molecule for downstream use.

51. Apparatus of claim 50 further including a detector within said housing, said ionized molecule passing from said plasma generator to said detector via said flow channel for downstream detection.

52. Apparatus of claim 51 further including an isolation means for isolating at least part of said electric field from contact with said ions and electrons.

53. Apparatus of claim 52 wherein at least one pair of electrodes defines at least a pair of tines, said at least one pair of electrodes mating via their tines interspersed for forming said plasma.

54. Apparatus of claim 52 further including RF resonant circuit drive means for diving said generator and forming said field.

55. Apparatus of claim 54 further including a feedback circuit for stabilizing plasma temperature.

56. A method for capacitively producing a discharge for ions, comprising:

passing a flowing supply through an RF electric field provided by cooperation of a first electrode and a second electrode in a manner resulting in forming a plasma therebetween, the plasma including ionized molecules; preventing said plasma from contacting some or all of said electrodes; and passing said ionized molecules out of said field.

57. The method of claim 56 wherein said flowing supply includes a flow of gas.

58. The method of claim 57 wherein said gas is air.

59 The method of claim 58 further comprising the step of generating said plasma at pressures including atmospheric pressure.

60. The method of claim 56 further comprising the step of driving said RF electric field with a resonant circuit to produce said plasma.

61. The method of claim 60 further comprising the step of stabilizing the energy level of said plasma by providing negative feedback to said resonant circuit.

62. The method of claim 61 further comprising the step of wherein said electrodes are made part of said resonant circuit.

63. The method of claim 56 further comprising the steps of providing an RF drive circuit and generating a packet waveform to drive the electrodes to generate said plasma.

64. The method of claim 56 further including the step of simultaneously generating positive and negative ions in said plasma.

65. A spectrometer for determining at least one compound in a sample, comprising:

an ionization source capacitively producing a discharge of ions, the ionization source having:

electrodes providing an electric field through which at least a portion of a carrier supply passes and by which forms a plasma having ions; and

an isolator for isolating at least part of at least one of said electrodes from having contact with said ions; and

means for introduction of at least one compound into said plasma for ionization, and

apparatus for determining the composition of said at least one compound ionized by said plasma.

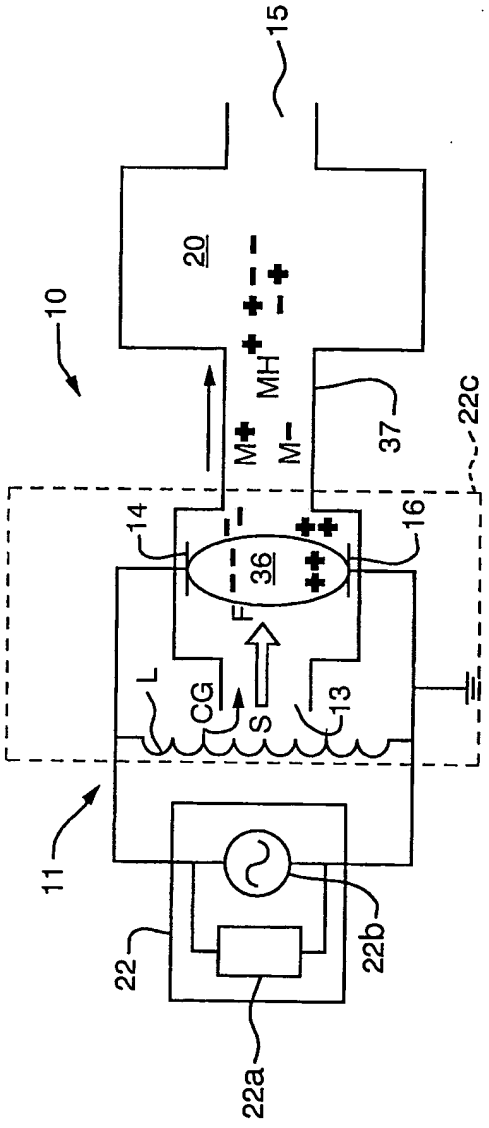


FIG. 1A

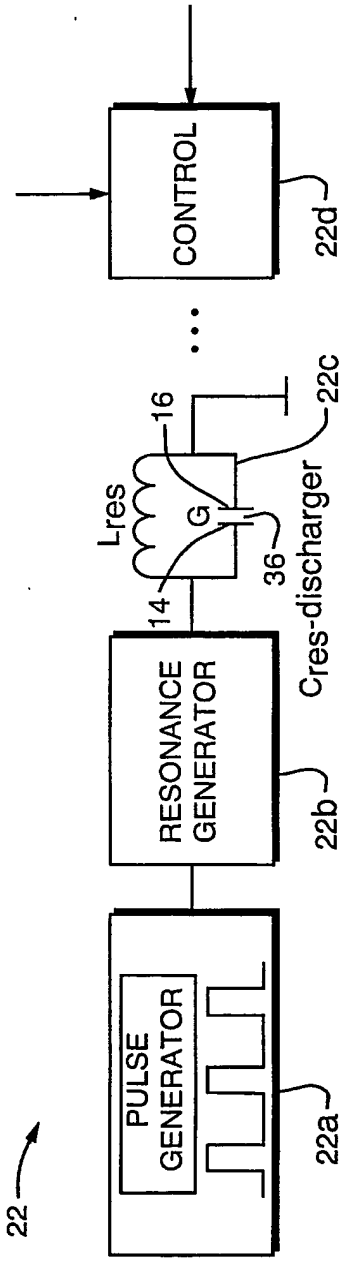

CONTROL
22d
16
22c
Lres
G
36
14
Cres-discharger
RESONANCE GENERATOR
22b
PULSE GENERATOR
22a
22

FIG. 1B

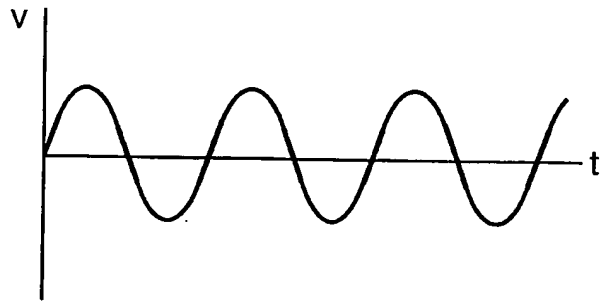


FIG. 1C

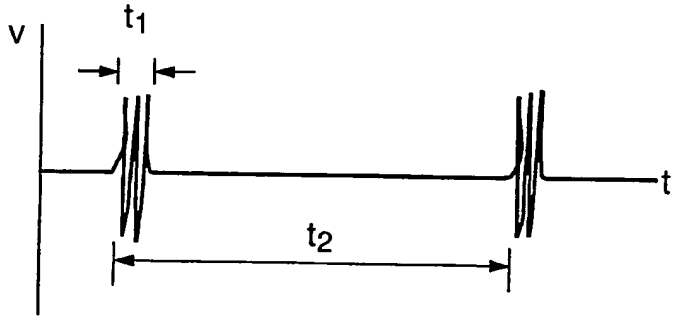


FIG. 1D

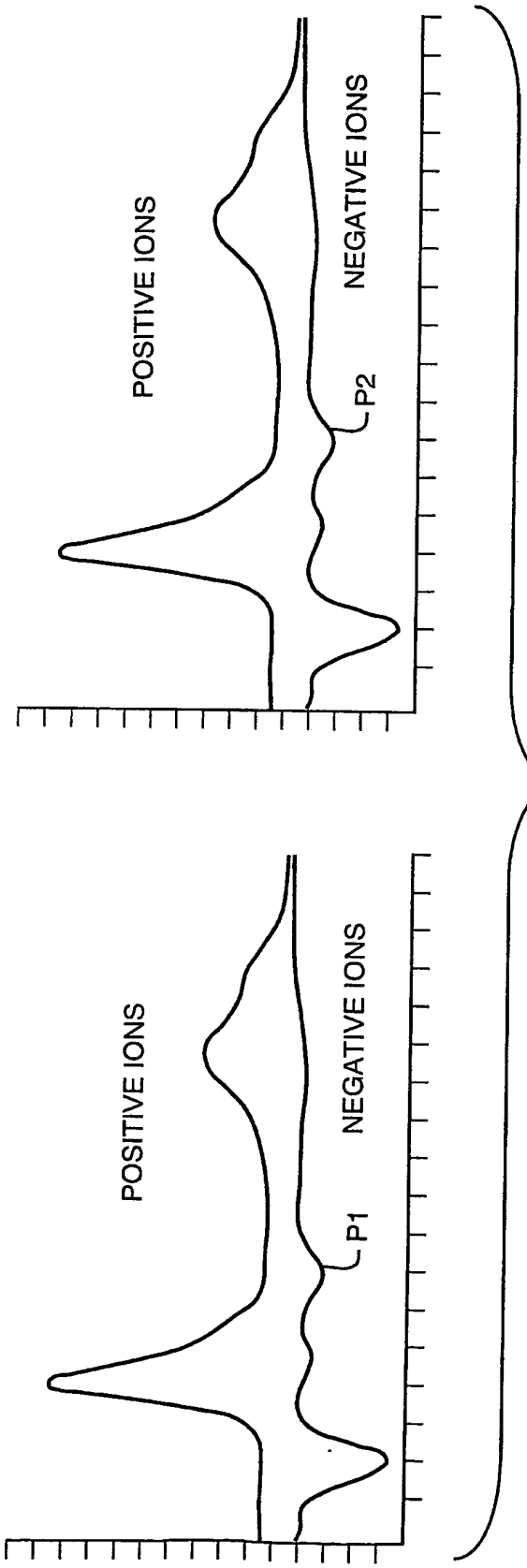

POSITIVE IONS
NEGATIVE IONS
P2
POSITIVE IONS
NEGATIVE IONS
P1

FIG. 1E

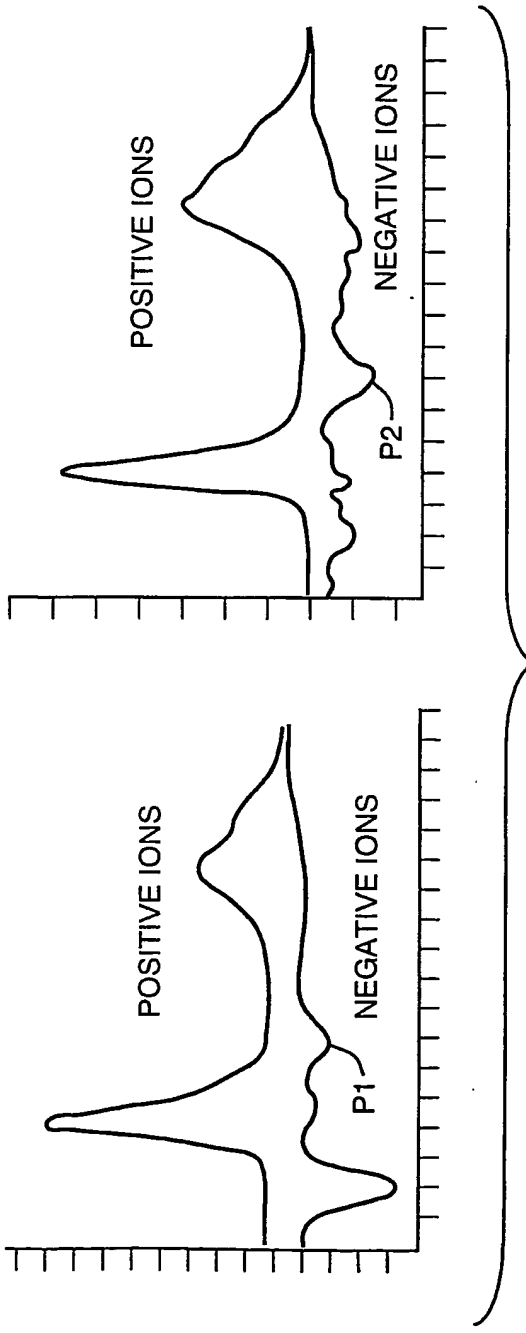
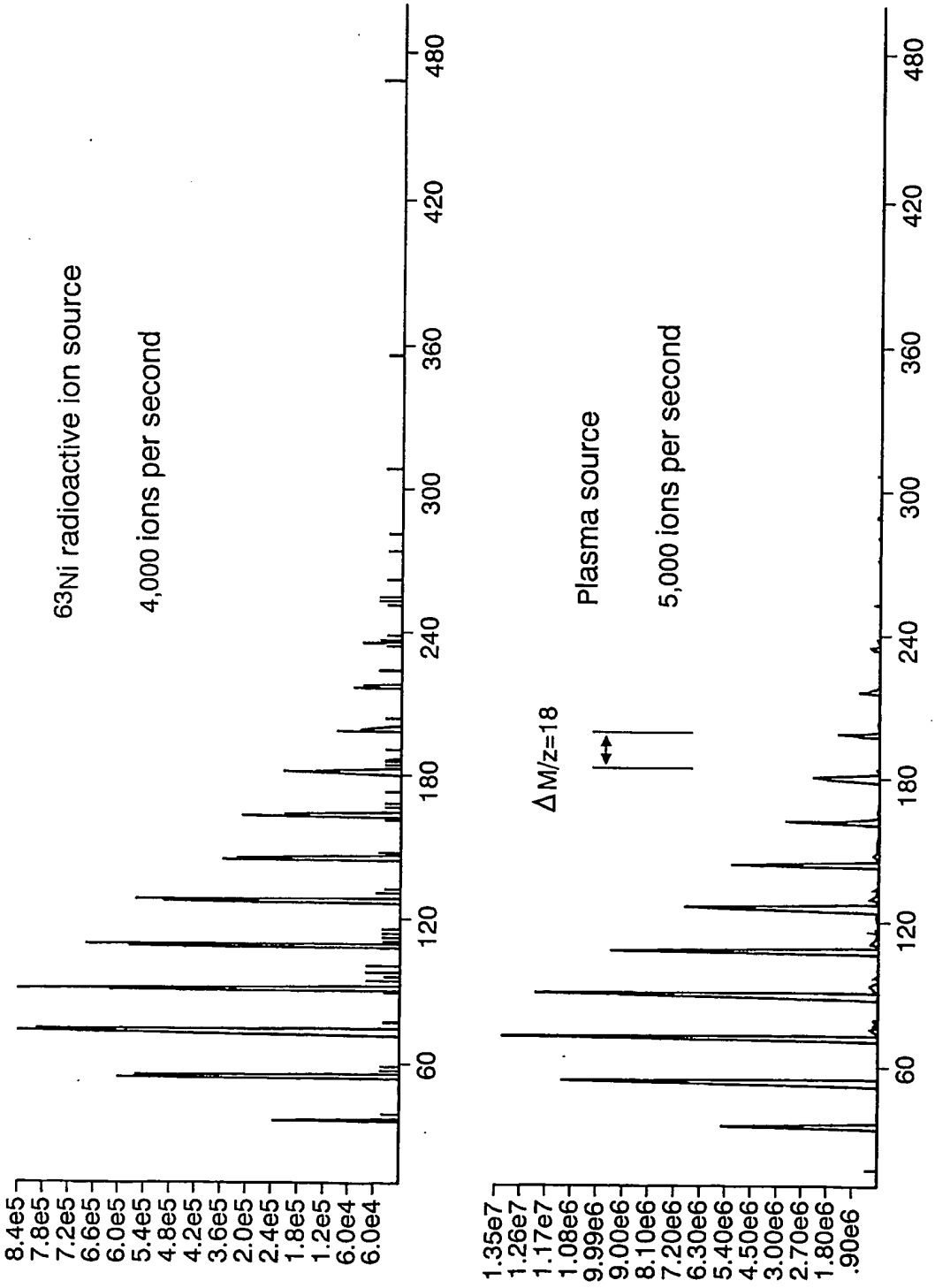

POSITIVE IONS
NEGATIVE IONS
P2
POSITIVE IONS
NEGATIVE IONS
P1

FIG. 1F


^{63}Ni radioactive ion source
4,000 ions per second
8.4e5
7.8e5
7.2e5
6.6e5
6.0e5
5.4e5
4.8e5
4.2e5
3.6e5
3.0e5
2.4e5
1.8e5
1.2e5
6.0e4
6.0e4
60
120
180
240
300
360
420
480
ΔM/z=18
Plasma source
5,000 ions per second
1.35e7
1.26e7
1.17e7
1.08e6
9.99e6
9.00e6
8.10e6
7.20e6
6.30e6
5.40e6
4.50e6
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60
120
180
240
300
360
420
480

FIG. 1G

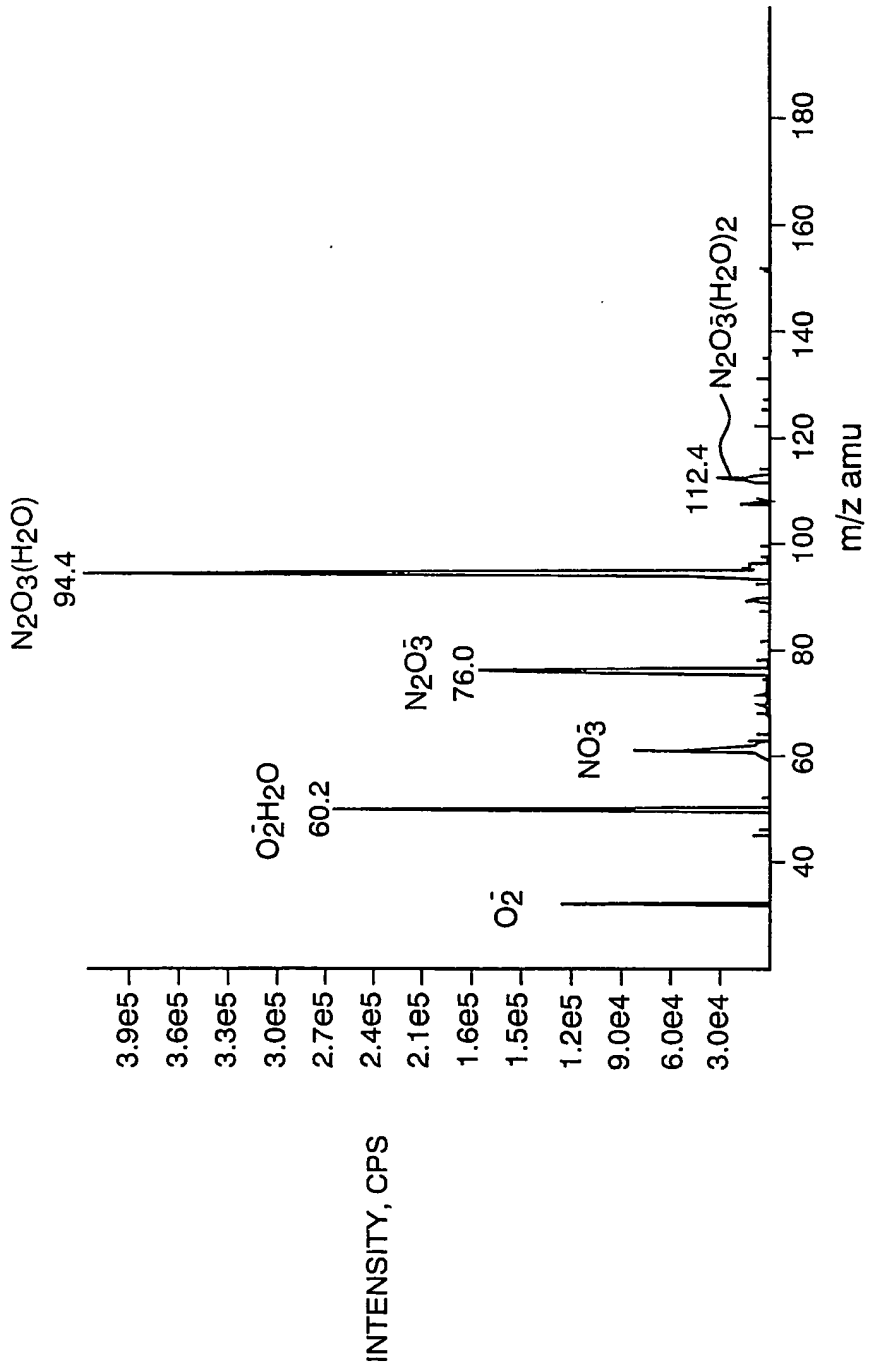

INTENSITY, CPS
3.9e5
3.6e5
3.3e5
3.0e5
2.7e5
2.4e5
2.1e5
1.6e5
1.5e5
1.2e5
9.0e4
6.0e4
3.0e4
40
60
80
100
120
140
160
180
m/z amu
O_2^-
$O_2^-H_2O$
60.2
NO_3^-
$N_2O_3^-$
76.0
$N_2O_3(H_2O)$
94.4
112.4
$N_2O_3^-(H_2O)_2$

FIG. 1H(1)

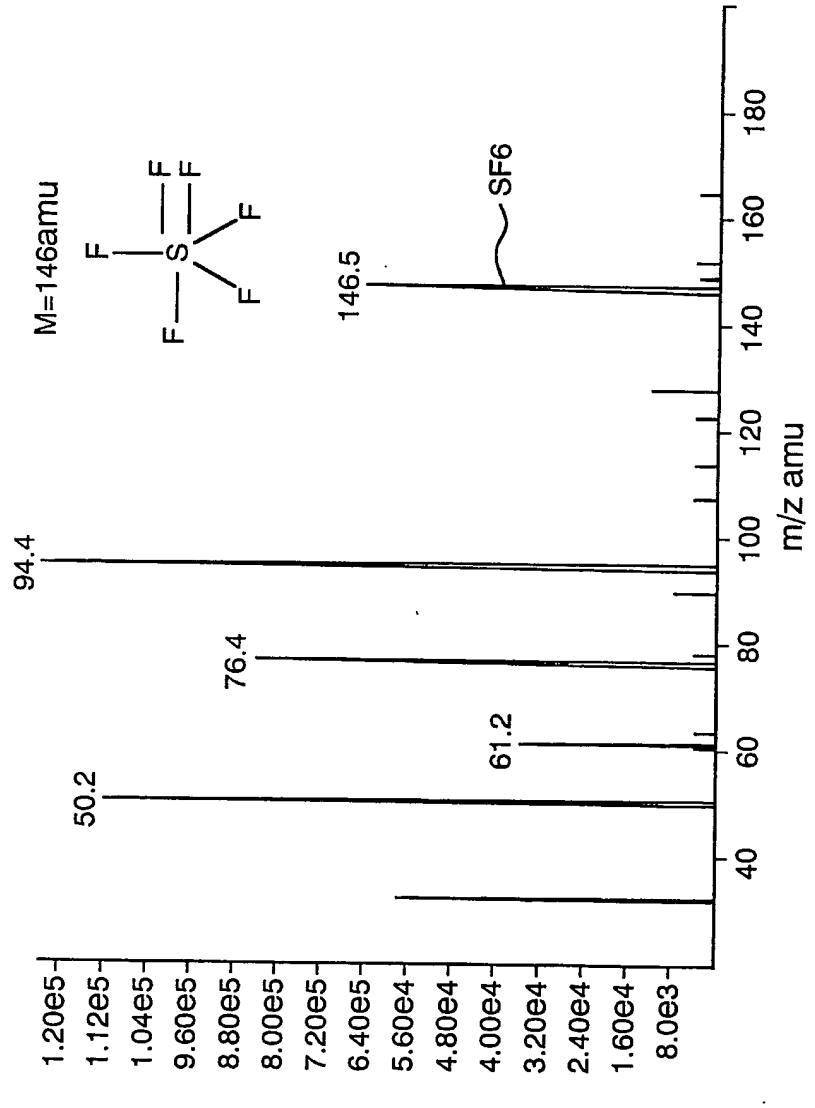

M=146amu
F
S
F
F
F
F
SF6
146.5
94.4
76.4
61.2
50.2
1.20e5
1.12e5
1.04e5
9.60e5
8.80e5
8.00e5
7.20e5
6.40e5
5.60e4
4.80e4
4.00e4
3.20e4
2.40e4
1.60e4
8.0e3
40
60
80
100
120
140
160
180
m/z amu

FIG. 1H(2)

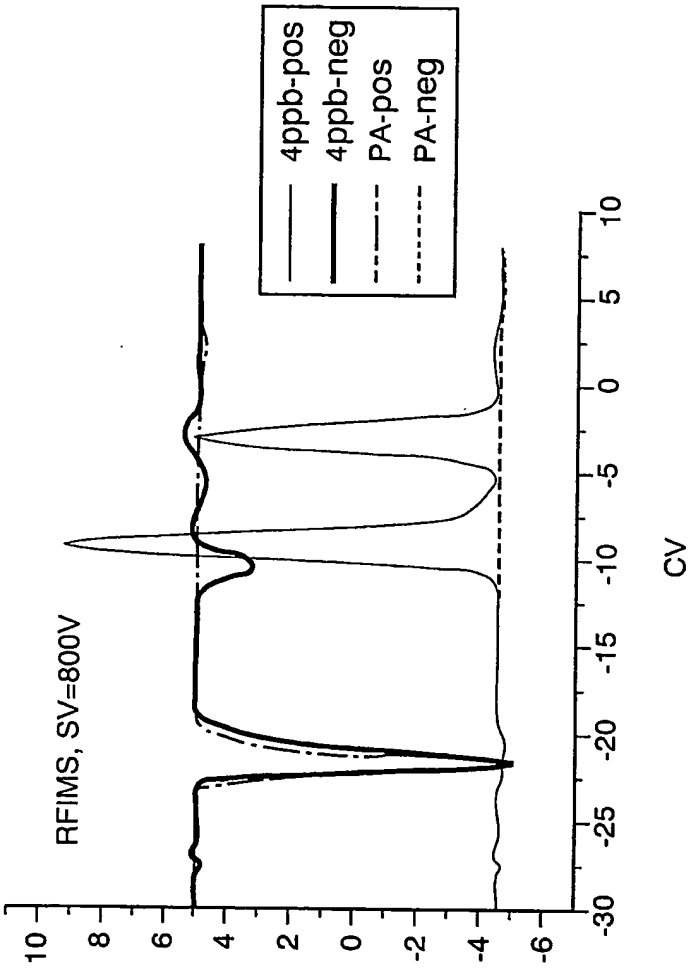

4ppb-pos
4ppb-neg
PA-pos
PA-neg
RFIMS, SV=800V
CV
10
8
6
4
2
0
-2
-4
-6
10
5
0
-5
-10
-15
-20
-25
-30

FIG. 1I

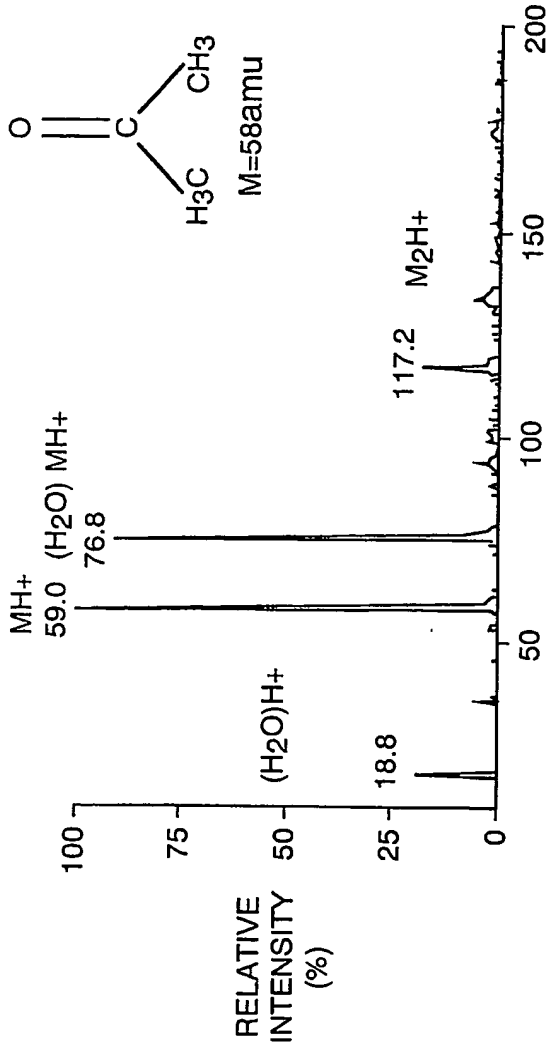

O
C
CH3
H3C
M=58amu
MH+
59.0
(H2O) MH+
76.8
(H2O)H+
18.8
117.2
M2H+
RELATIVE INTENSITY (%)
100
75
50
25
0
50
100
150
200
m/z

FIG. 1J

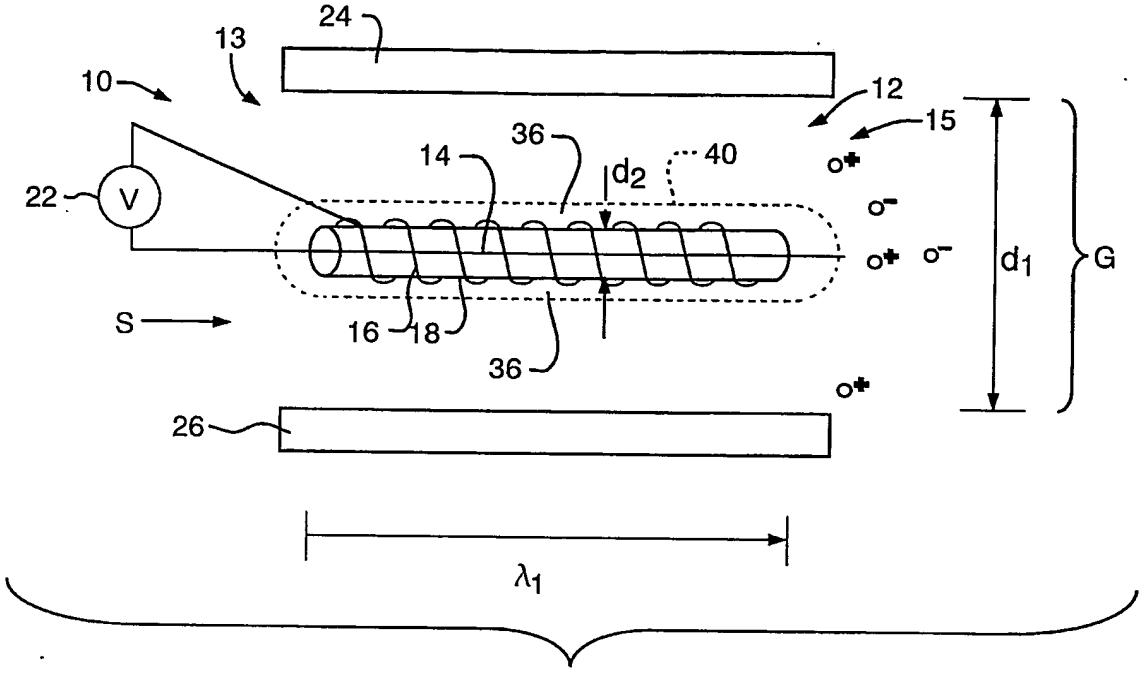

24
13
10
12
15
36
14
40
d_2
22
V
d_1
G
S
16
18
36
26
λ_1

FIG. 2A

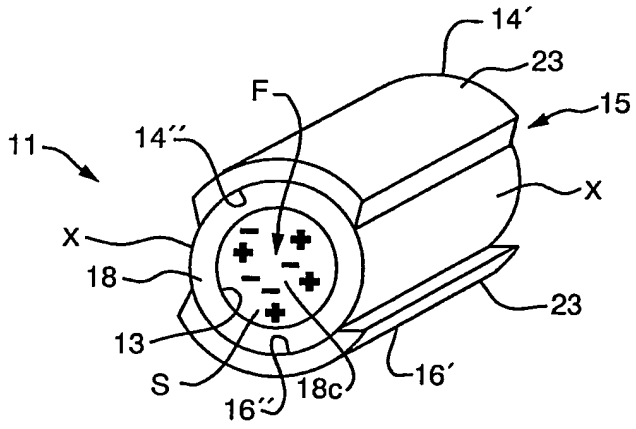

14′
23
F
15
11
14″
X
X
18
23
13
S
16″
18c
16′

FIG. 2B

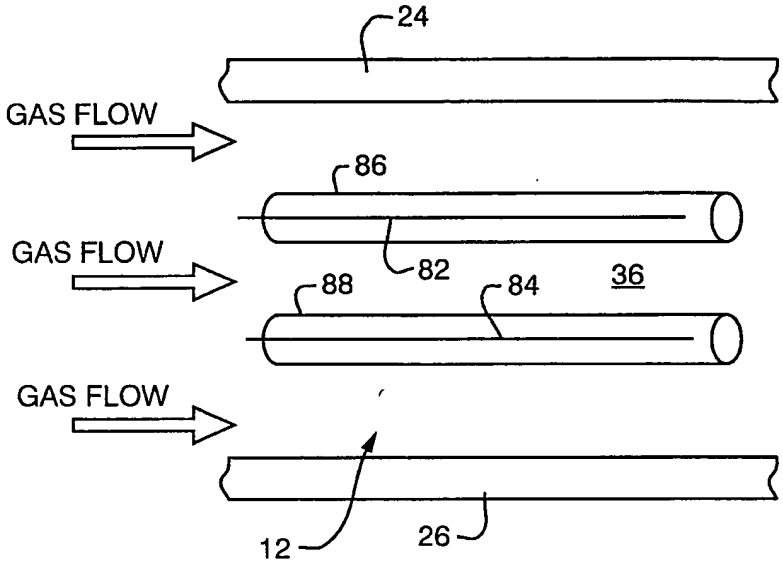
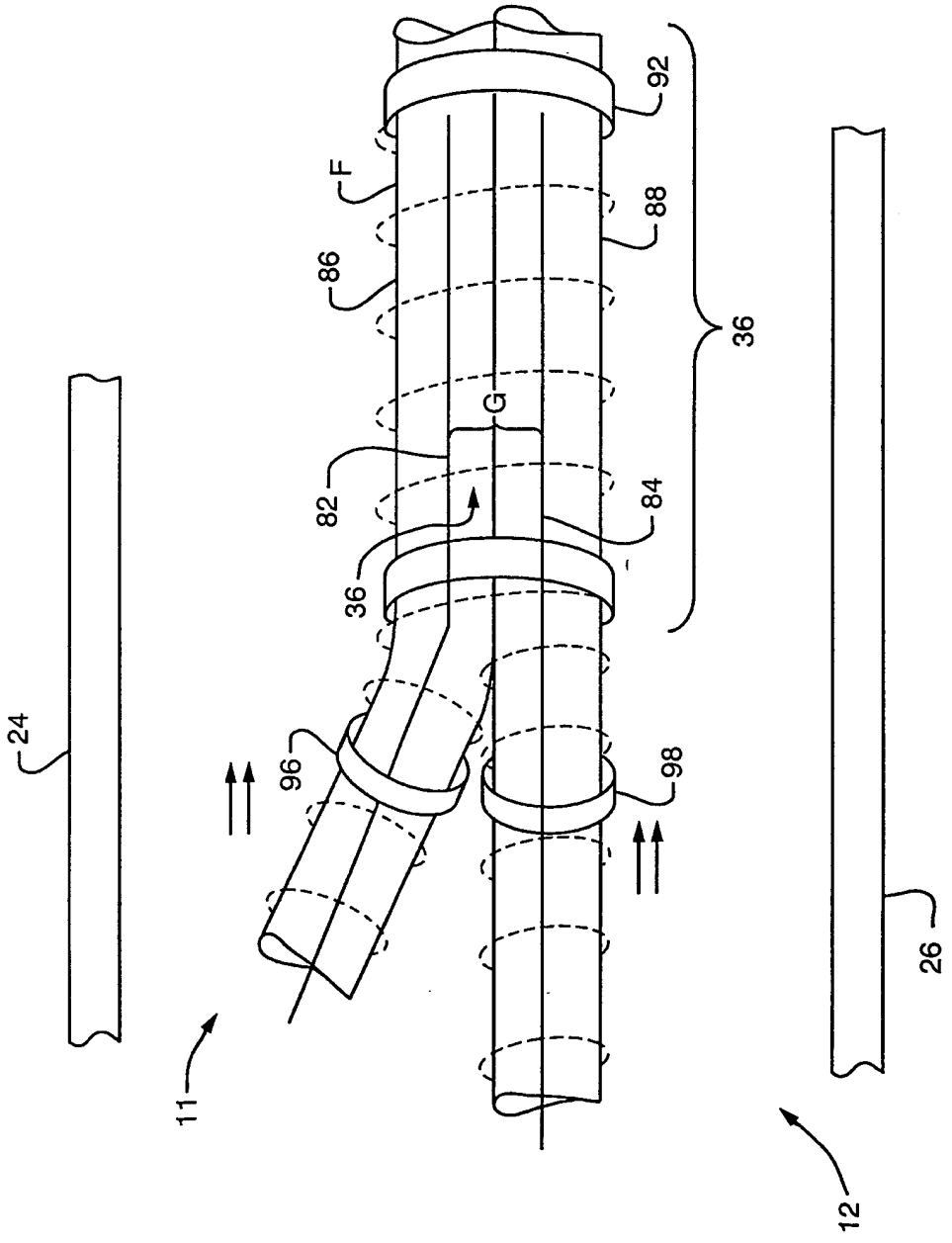


FIG. 2C

FIG. 2D



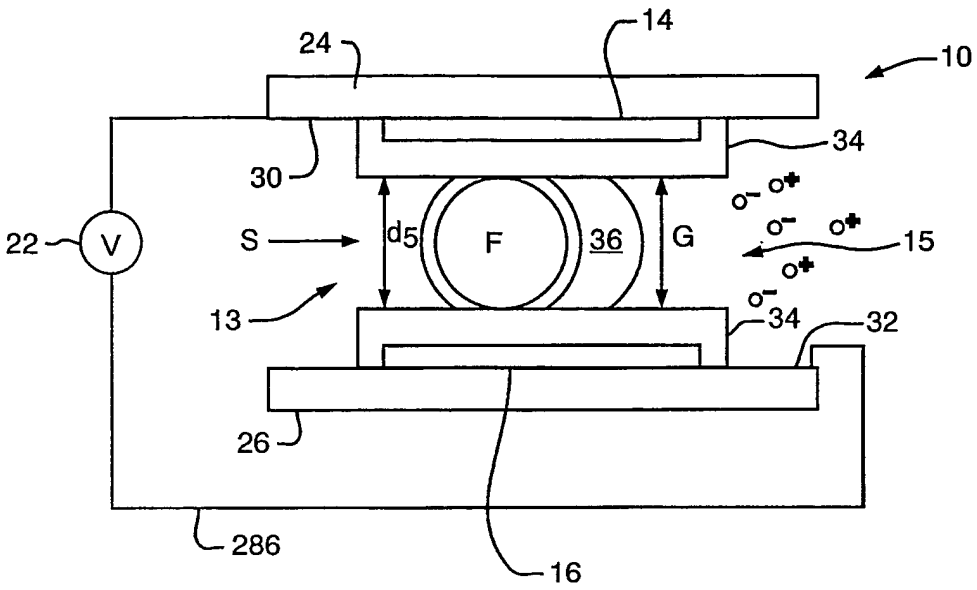


FIG. 3

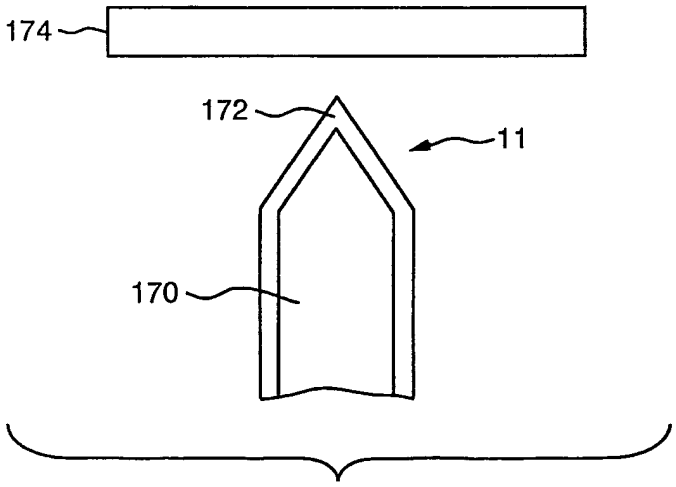


FIG. 4

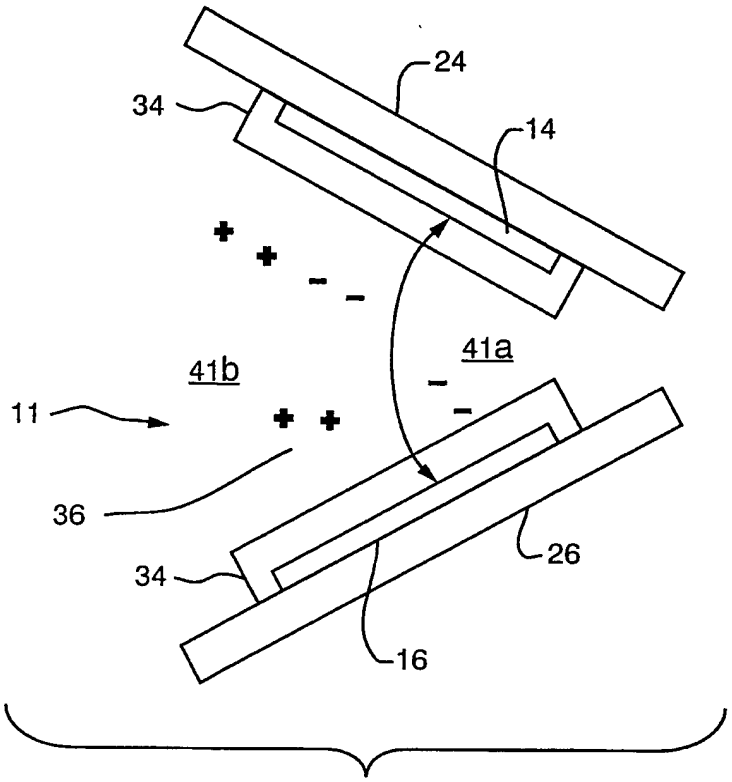


FIG. 7

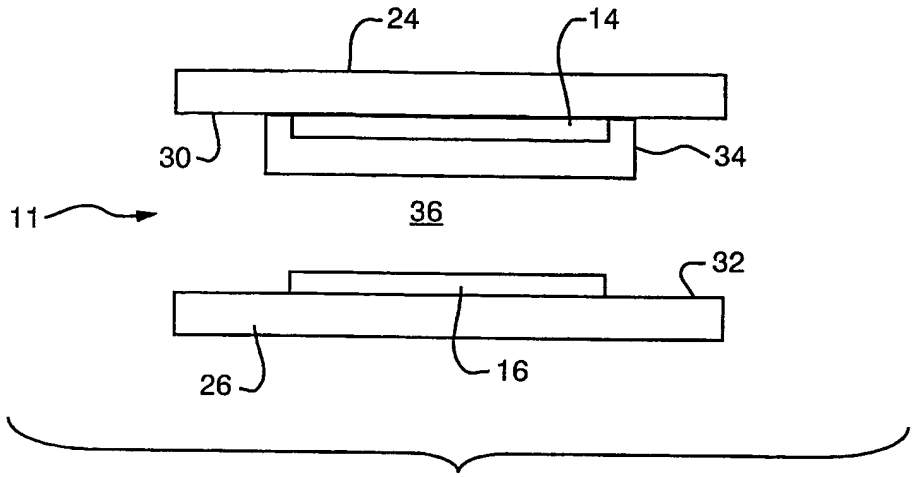


FIG. 8

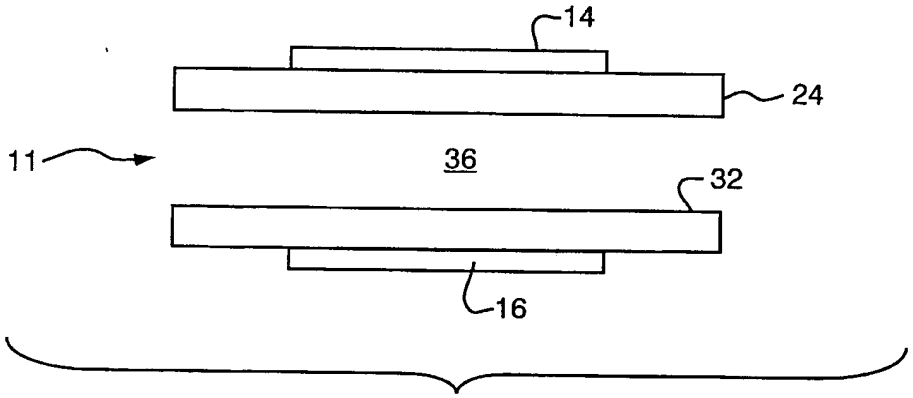


FIG. 9

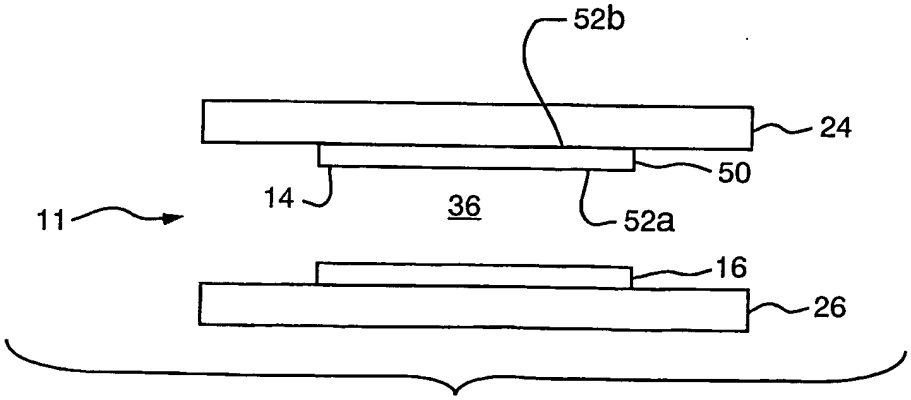


FIG. 10

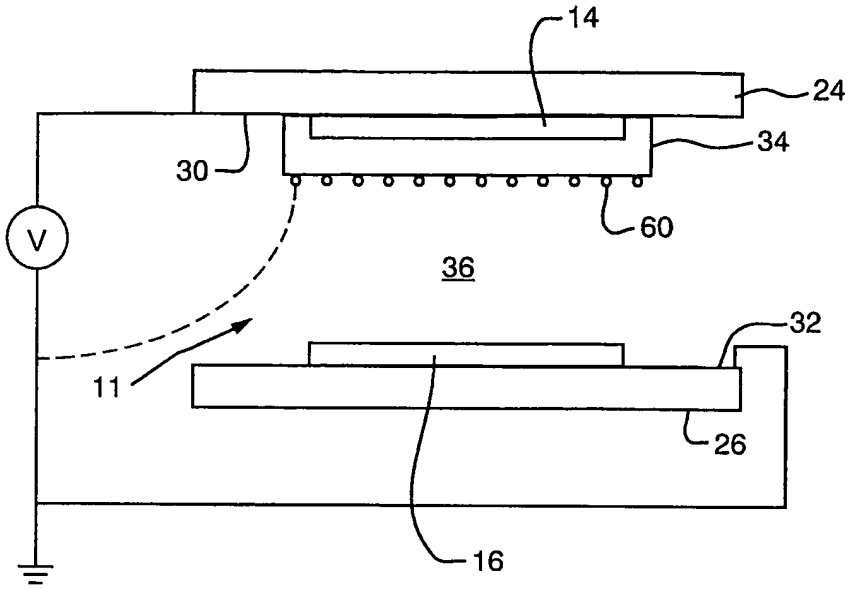


FIG. 11

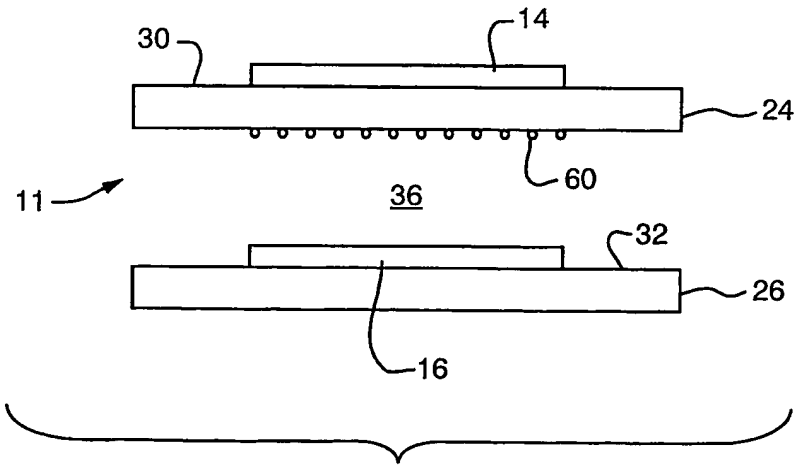


FIG. 12

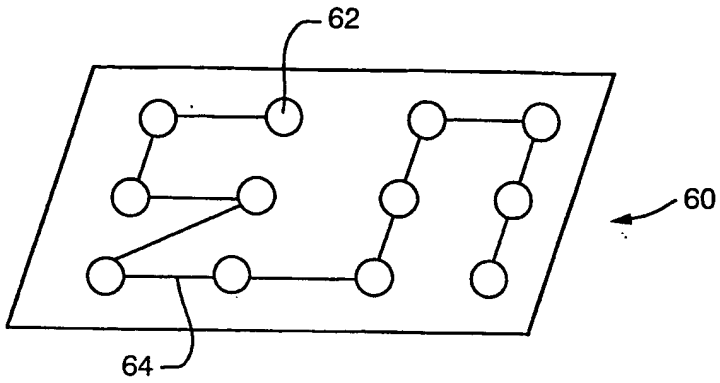


FIG. 13A

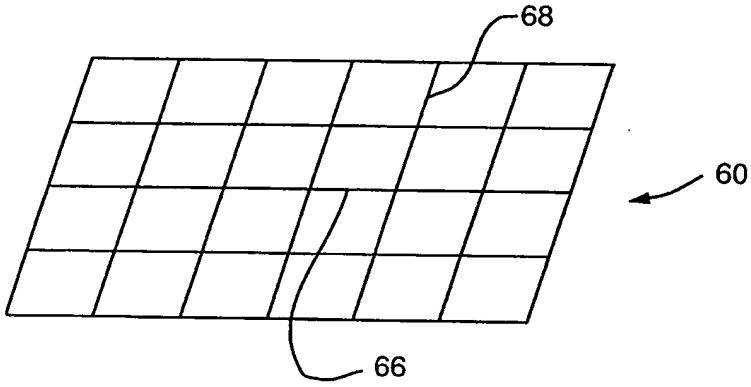


FIG. 13B

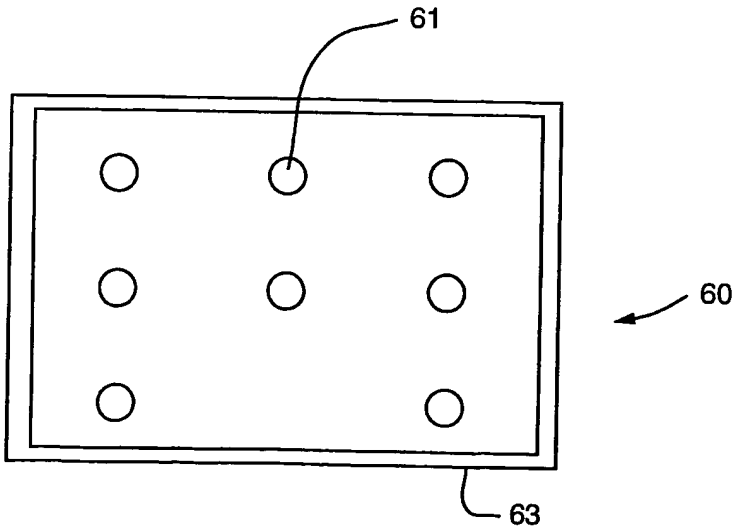


FIG. 13C

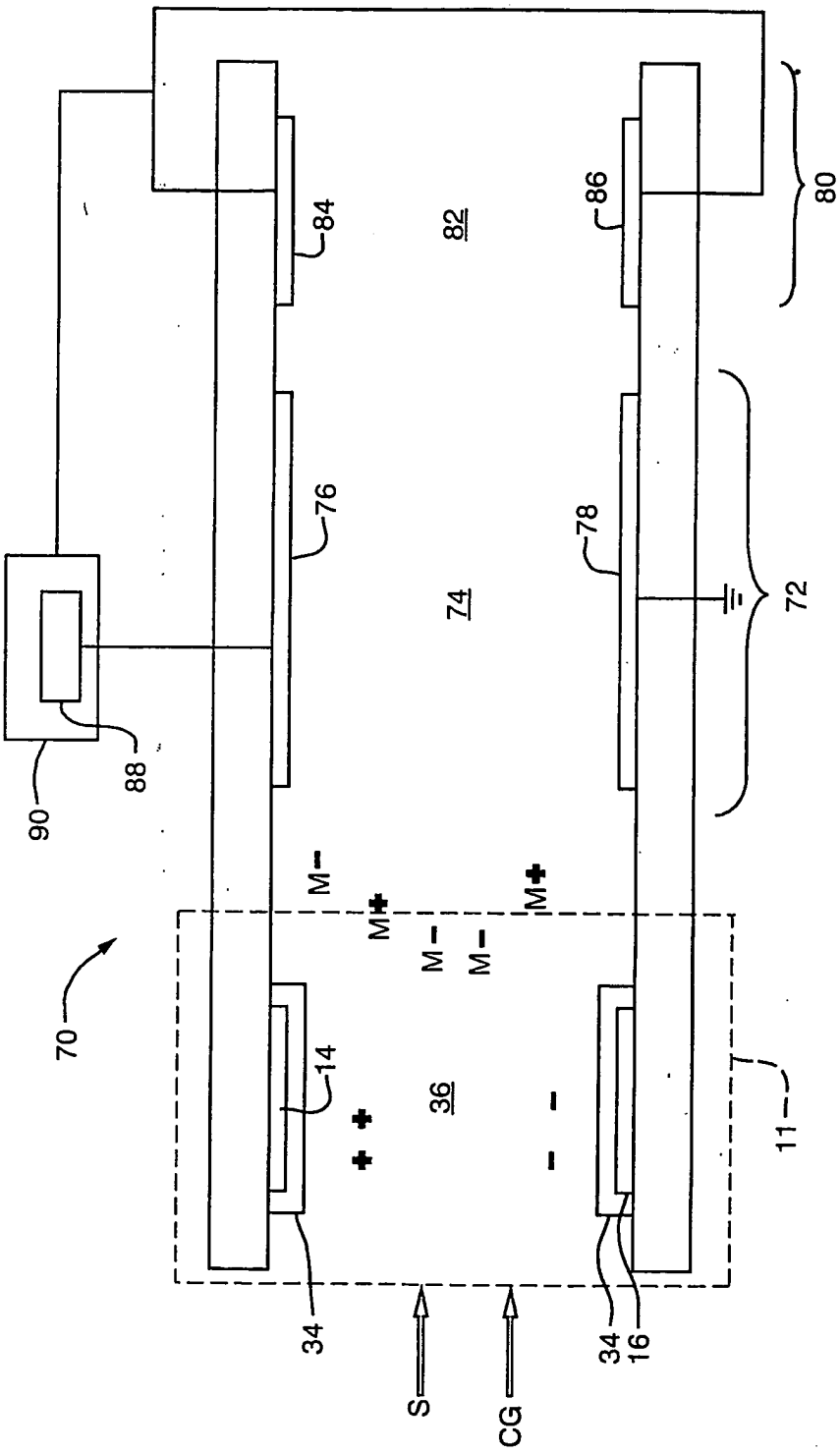


FIG. 14A

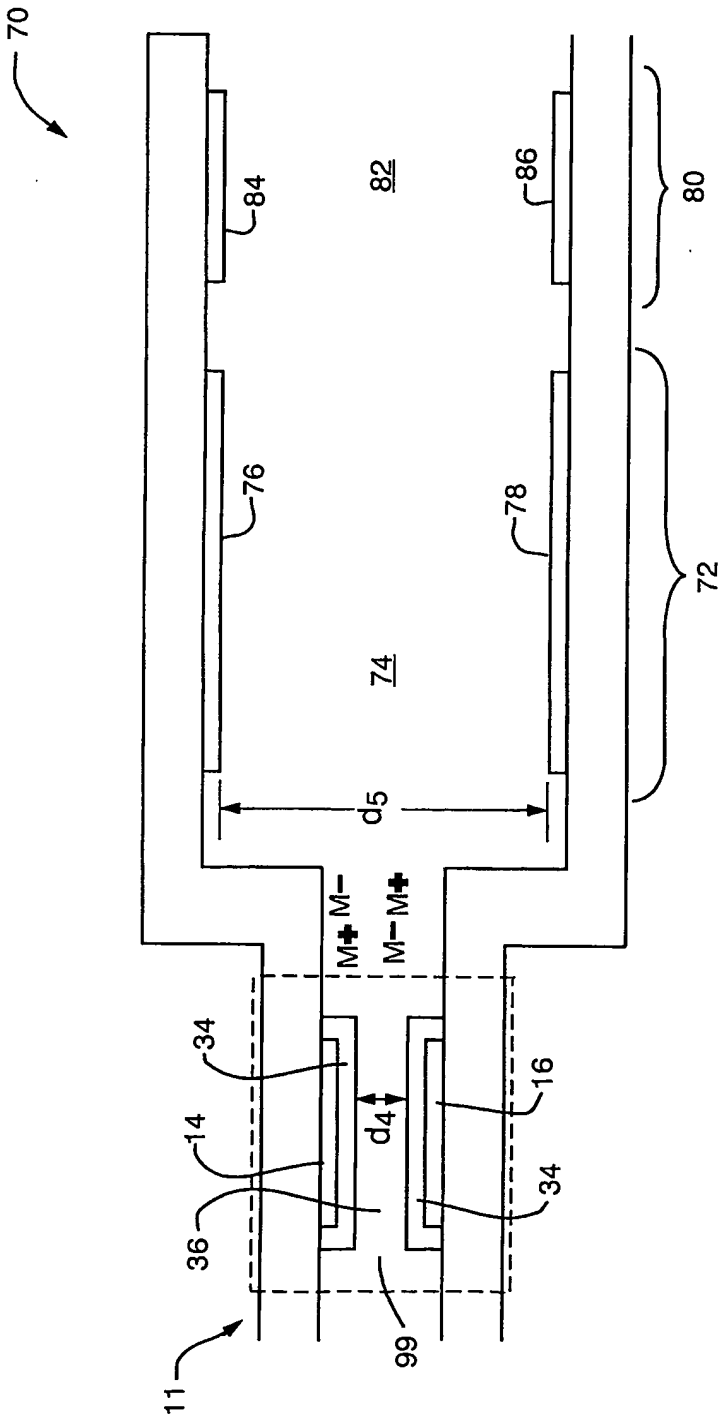


FIG. 14B

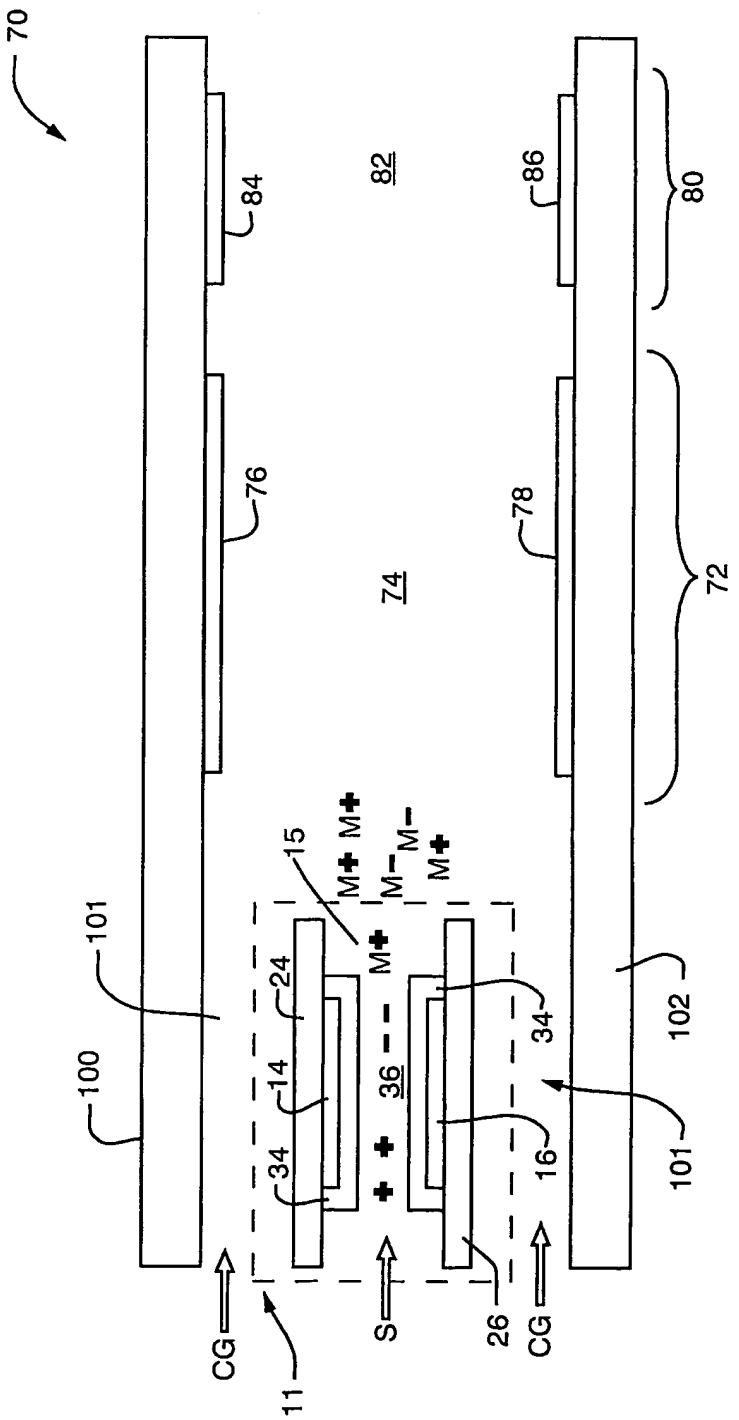

70
84
82
86
80
76
74
78
72
101
15
M+ M+
M- M-
M+
24
M+
100
14
36
34
34
16
102
101
CG
S
26
CG
11

FIG. 14C

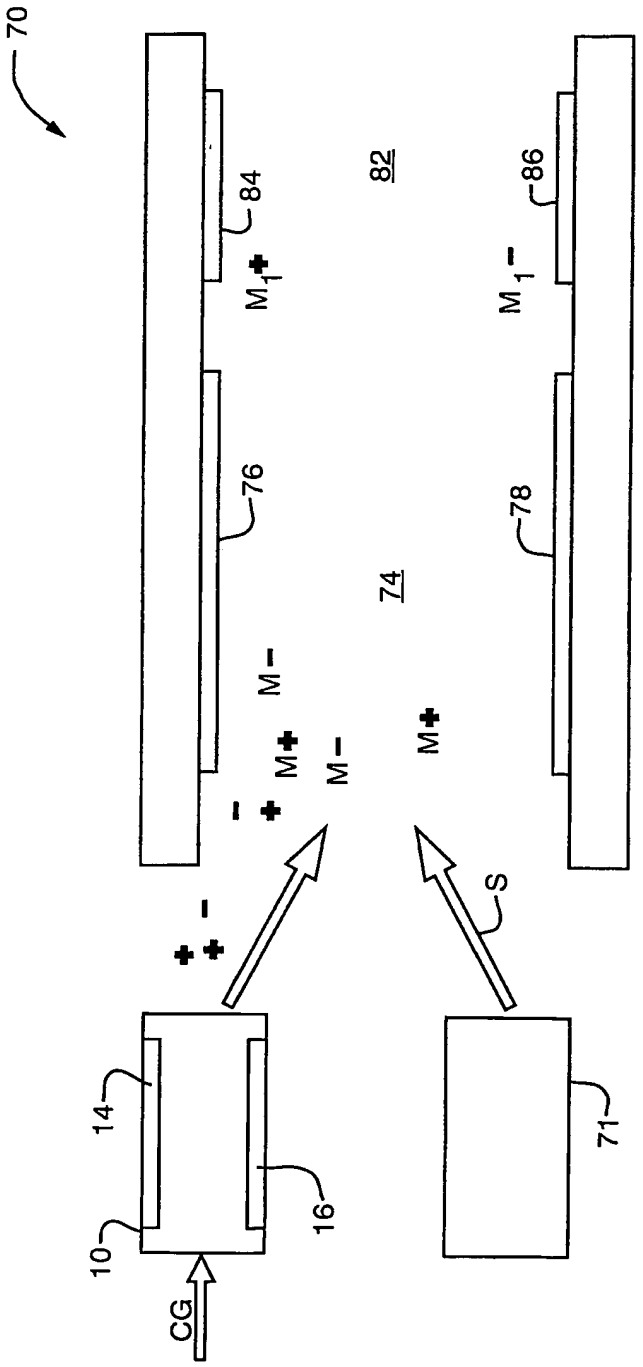


FIG. 14D

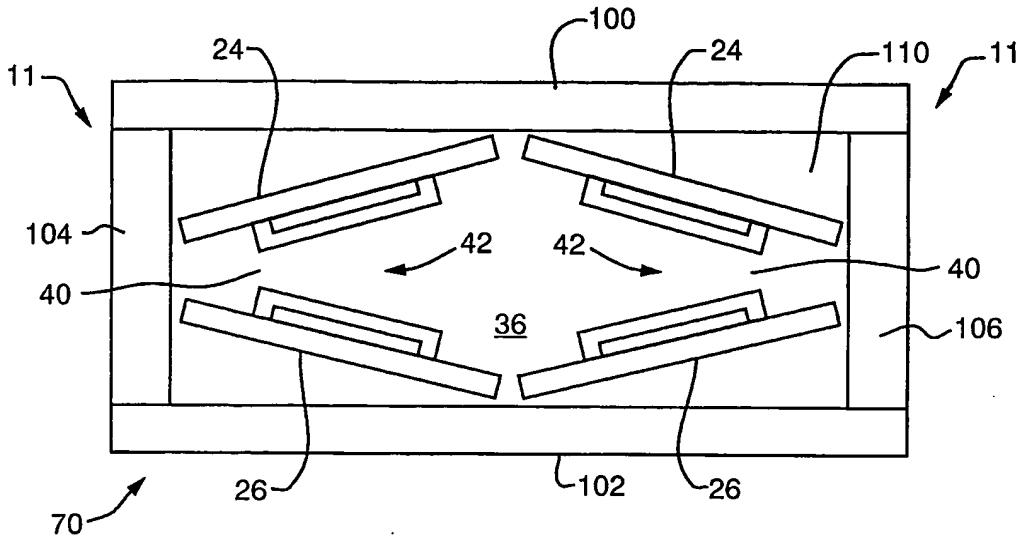


FIG. 15A

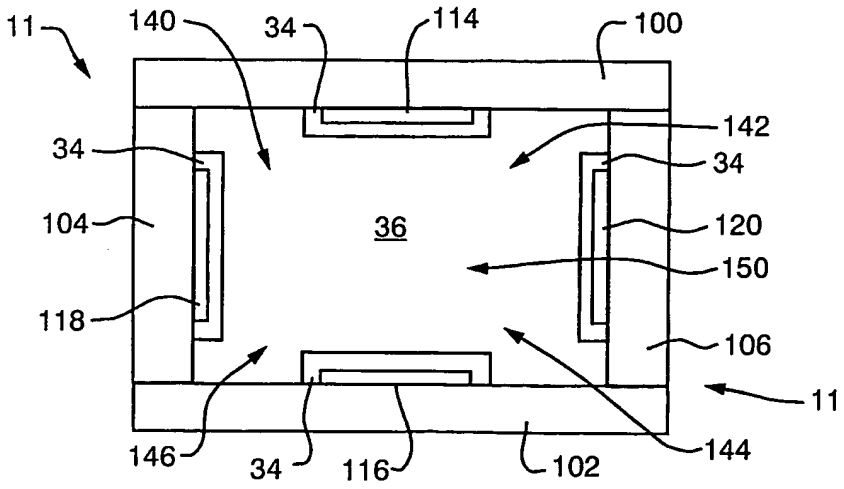


FIG. 15B

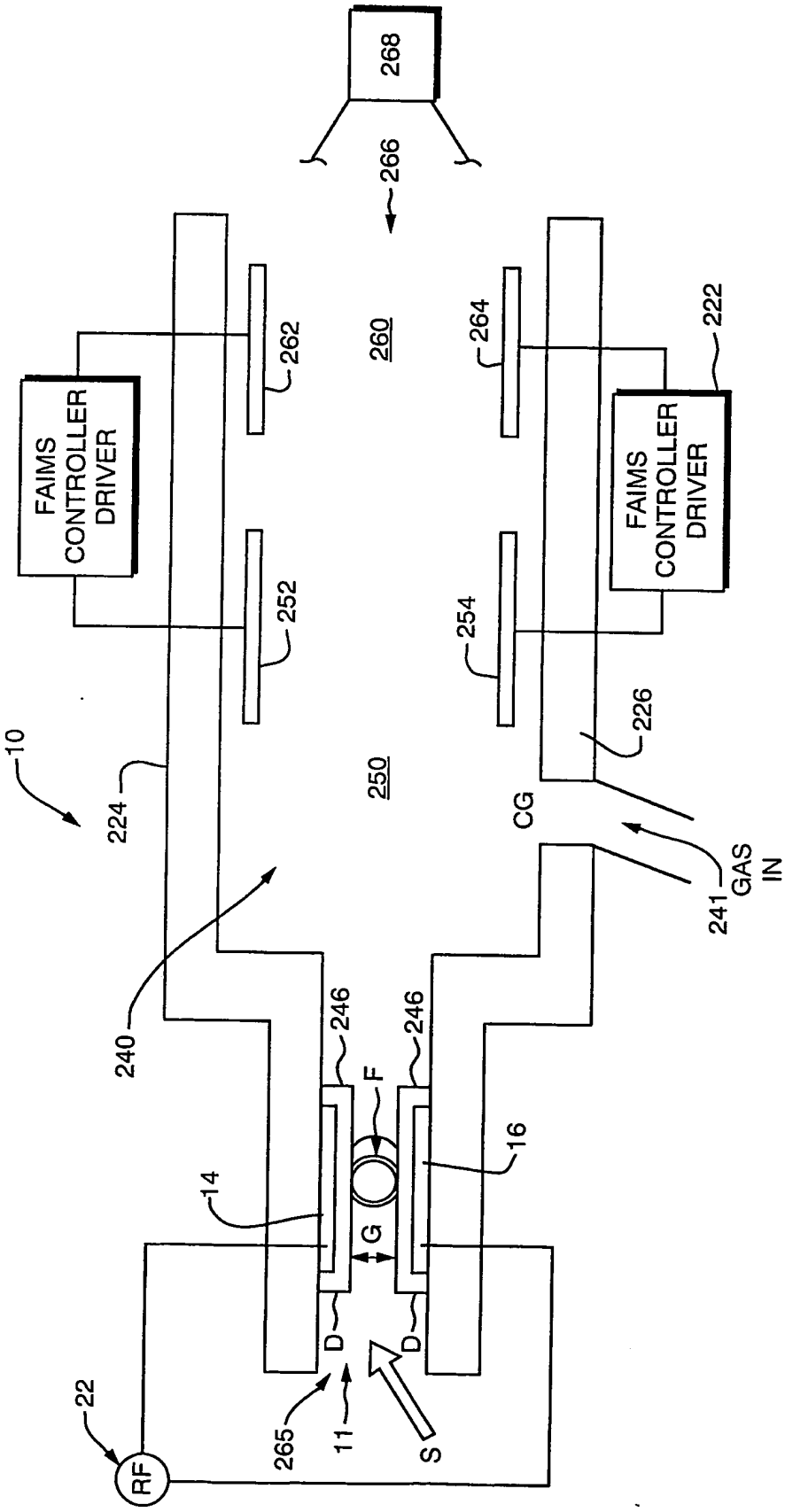

268
266
260
262
264
222
FAIMS CONTROLLER DRIVER
FAIMS CONTROLLER DRIVER
252
254
10
224
250
226
CG
GAS IN
241
240
246
246
F
16
14
G
D
D
22
RF
265
11
S

FIG. 16

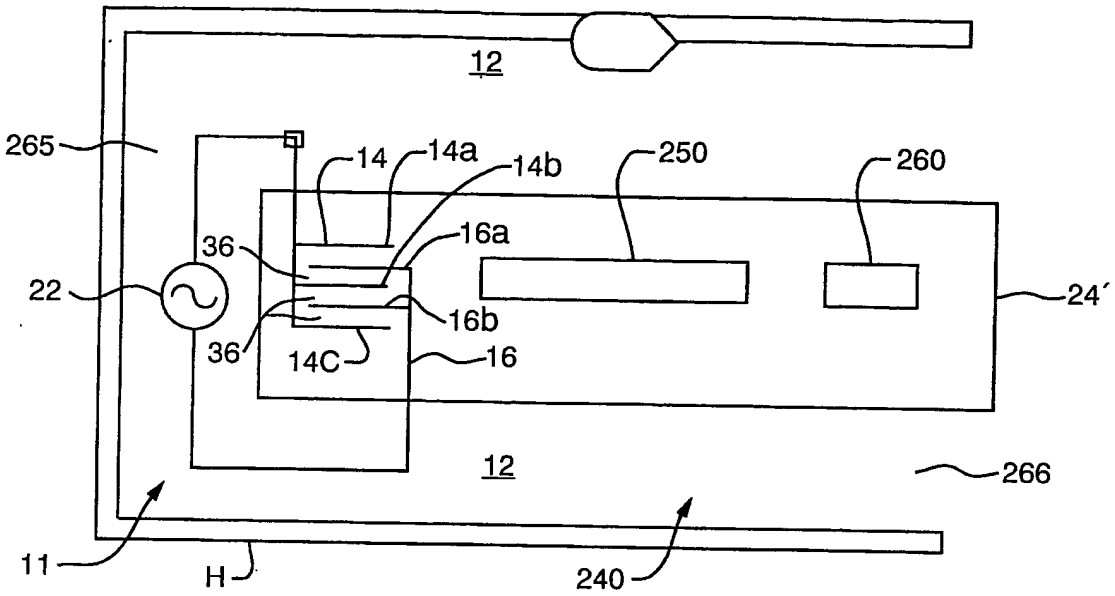


FIG. 17A

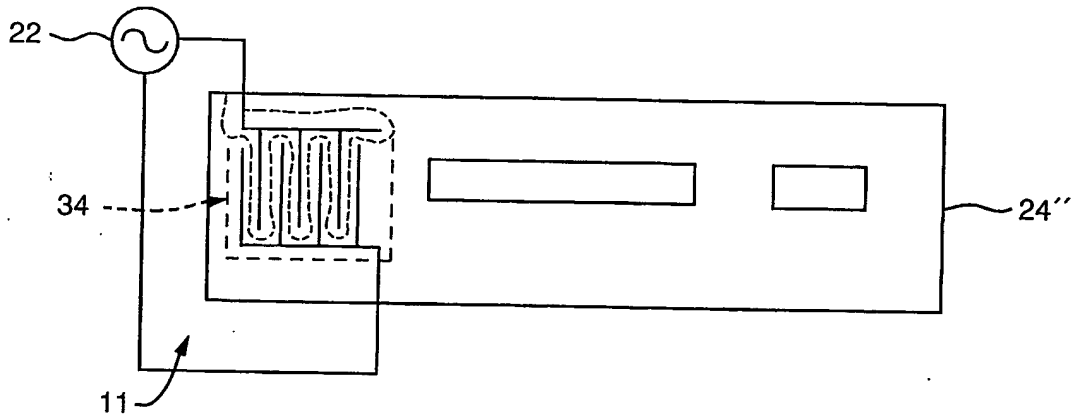


FIG. 17B

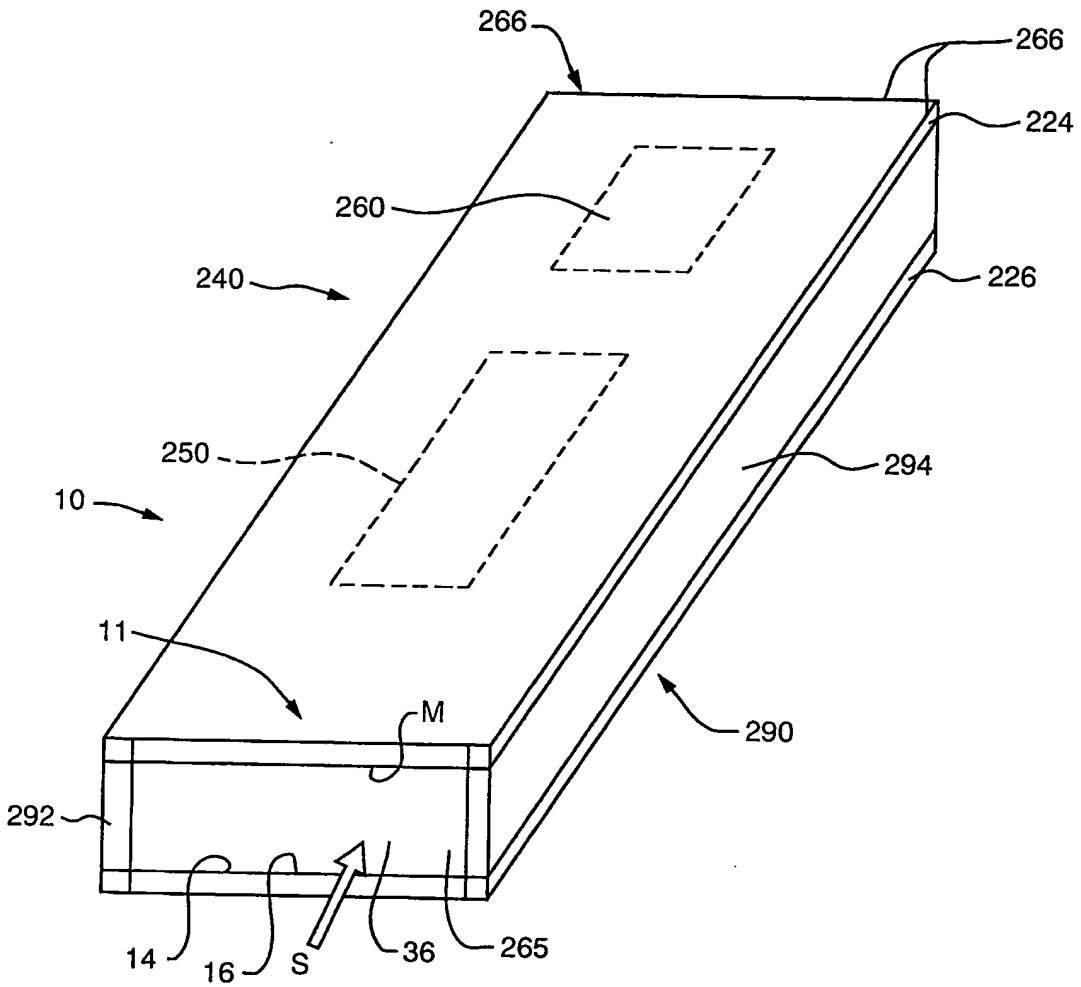


FIG. 17C

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US02/25190

A. CLASSIFICATION OF SUBJECT MATTER
IPC(7) : H01J 27/00; H01S 3/22; H05B 31/22
US CL : 315/337, 359, 169R; 331/94.5; 313/231.6
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 315/337, 359, 169R; 331/94.5; 313/231.6

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
None

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
None

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,201,921 A (McCORKLE) 06 May 1980 (06.05.1980), see entire document.	1-65
Y	US 4,025,818 A (GIGUERE et al.) 24 May 1977 (24.05.1977), see entire document.	1-65
Y	US 3,931,589 A (AISENBERG et al.) 06 January 1976 (06.01.1976), see entire document.	1-65

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 November 2002 (29.11.2002)	23 DEC 2002
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703)305-3230	Authorized officer Don Wong Telephone No. 703-308-4856

Form PCT/ISA/210 (second sheet) (July 1998)